Progress Quantum Electronics Volume 2

Editors: J. H. Sanders and S. Stenholm

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Part 3

Collision Broadening of Spectral Lines by Neutral Atoms

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Pergamon Press

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COLLISION BROADENING OF SPECTRAL LINES BY NEUTRAL ATOMS

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BY

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PERGAMON PRESS

OXFORD · NEW YORK · TORONTO
SYDNEY · BRAUNSCHWEIG

PERGAMON PRESS LTD.
Headington Hill Hall, Oxford
PERGAMON PRESS INC.
Maxwell House, Fairview Park, Elmsford, New York 10523
PERGAMON OF CANADA LTD.
207 Queen's Quay West, Toronto 1
PERGAMON PRESS (AUST.) PTY. LTD.
19a Boundary Street, Rushcutters Bay, N.S.W. 2011, Australia
VIEWEG & SOHN GmbH
Burgplatz 1, Braunschweig

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First edition 1972

Library of Congress Catalog Card No. 70–13569

Printed in Great Britain by A. Wheaton & Co., Exeter

08 016881 7

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1. INTRODUCTION

The serious study of the phenomenon commonly known as the pressure broadening of spectral lines is now over three-quarters of a century old. It was in 1895 that Michelson made the first important contribution to this subject, and identified the mechanism of pressure broadening as the sudden interruption of the vibrations of the atomic radiation by collisions with neighbouring atoms. A simple Fourier analysis then shows that the line width is of the order $1/\bar{\tau}$ where $\bar{\tau}$ is the mean time between collisions. This fundamental idea was followed up by Lorentz (1906) who concentrated his attention on absorption rather than emission and showed that the effect of random sudden collisions is equivalent to an additional damping force, proportional to velocity, exerted on the atomic oscillators. The line profile then has the well-known Lorentzian shape.

A quite different approach to pressure broadening was initiated by Debye (1919) and Holtsmark (1919) in the context of perturbation of the radiating atom by charged particles. Here the environment of the radiator is considered to exert a slowly changing influence on the frequency emitted, and the intensity profile of the spectral line is given by the probability of occurrence of the configurations of perturbers which give the various frequency displacements. The application of this idea to broadening by neutral particles was made by Jablonski (1931) and, in more detail, by Margenau (1932). This type of treatment of the problem is known as quasi-static (or statistical) theory.

Important progress was made by Weisskopf (1932, 1933), who perceived that the nature of the interruption of the atomic oscillations visualized by Michelson and Lorentz was essentially an interruption of phase. If the phase change induced by the collision is greater than a certain critical value, which Weisskopf took to be 1 radian, then the wave train is effectively terminated, and it is the mean time between such "strong" collisions which determines the width of the resulting Lorentzian profile. If the interaction potential between the perturbing and radiating atoms is known, it is possible to calculate the line width. Weisskopf further showed that a simple quantum mechanical calculation based on the same physical idea leads, in the WKB approximation, to the same result.

In another section of his wide-ranging review, Weisskopf (1933) discussed the relationship between the two apparently different approaches to pressure broadening. The interruption, or impact, approach entirely neglects the radiation emitted during a collision, while the quasi-static approach takes into account radiation emitted at all times but does not make a Fourier analysis and consequently is a low velocity limit of a more general theory.

Since the work of Weisskopf, progress in the theoretical understanding of pressure broadening caused by neutral atoms has developed along four main lines:

(1) The impact theory for classical atomic oscillators has been completely developed, taking account of collisions which induce small phase changes ("weak" collisions) as well as those which induce large phase changes ("strong" collisions). The former collisions give rise to a shift of the spectral line, which, however, remains Lorentzian in shape (Lenz, 1933; Lindholm, 1945; and Foley, 1946).

(2) Attempts have been made to develop a quite general classical theory which includes the impact and quasi-static approximations as limiting cases. Lindholm (1945) achieved an approximate solution to this problem. Other attempts are referred to in the earlier review articles mentioned below, and recent attempts are discussed in section 2C of this article.

(3) The quantum mechanical theory of impact broadening has been the subject of many contributions in recent years. An early attempt to establish the general formalism by Spitzer (1940) was followed by further elucidation by Anderson (1949), Baranger (1962) and Griem (1964), and from a different point of view by Fano (1961). Resonance broadening (where the perturbing and radiating atoms are of the same species and can exchange excitation energy in a collision) has attracted a great deal of attention, and important contributions have been made

by Byron and Foley (1964), Omont (1966), Mead (1960) and Ali and Griem (1965, 1966). Some of these matters form the subject of section 2B of this review.

(4) In the field of "foreign" gas broadening, with which this article is mainly concerned, developments have largely centred on the question of the interatomic potential. The use of the Lennard-Jones potential has been explored in the impact approximation by Behmenburg (1964) and by Hindmarsh and co-workers (1963, 1967), and in the quasi-static approximation by Bergeon, Robin and Vodar (1952) and Bergeon (1954) and by Farr and Hindmarsh (1968). Section 2C of the present work is devoted to these developments.

The most important of the previous reviews of this subject is that of Ch'en and Takeo (1957). This provides a comprehensive account of both experimental and theoretical work up to that date. In the present article we shall mention work earlier than 1957 only where it is necessary for understanding the later developments. Other useful reviews and books are by Sobelman (1954), Unsöld (1955), Traving (1960) and Breene (1957, 1961). The present work does not aim at total comprehensiveness, but rather at establishing the present position achieved by theoretical and experimental investigation.

2. THEORY

A. Classical Theory of Collision Broadening

1. *General formulation*

The classical model represents an atomic radiator as an elastically bound oscillating electron, and the problem of collision broadening is to calculate the spectrum of such an oscillator when it is disturbed by collisions with the other atoms in its environment. We assume that the collisions do not change the amplitude of the oscillator, but only the phase. This is equivalent to assuming that the transition probability is unchanged by the collision. This seems on the whole to be confirmed by observation, at least at low pressures, although it has been suggested (e.g. Jefimenko, 1964) that in some cases it is incorrect. The evidence is not altogether clear, but all existing theories involve this assumption. The treatment of the classical problem which follows is largely based on that of van Trigt (1966) who even at that late date found that several points required clarification. The displacement of the oscillator as a function of time is given by

$$\mathrm{f}(t) = \mathrm{Re}\left[\exp\left\{i\int_0^t \omega'(t')\,\mathrm{d}t'\right\}\right],\ t > 0 \tag{1}$$

where $\omega'(t')$ is the instantaneous angular frequency of the oscillation at time t' and Re stands for "real part of". The undisturbed frequency will be represented by ω_0, and the oscillation begins at $t = 0$. The effect of natural damping is ignored. It is, in fact, often negligible compared with collisional effects, but in the impact approximation the effects of natural and collisional damping are additive, as Lorentz (1906) showed. The intensity profile $I\,(\omega)$ of the light emitted by the oscillator is then given by the squared modulus of the complex Fourier transform of $\mathrm{f}(t)$:

$$I(\omega) = \left|\int_0^\infty \left\{\mathrm{Re}\left[\exp\left\{i\int_0^t \omega'(t')\,\mathrm{d}t'\right\}\right]\right\} \exp\,\{i\omega t\}\,\mathrm{d}t\,\right|^2. \tag{2}$$

A more manageable, and entirely equivalent, general expression is found by first writing the autocorrelation function of the disturbance $\mathrm{f}(t)$. Putting

$$\int_0^t \omega'(t')\,\mathrm{d}t' = \omega_0 t + \eta(t)$$

where $\eta(t)$ is the departure in phase of the perturbed oscillation from the unperturbed oscillation, the autocorrelation function $\Phi(s)$ is:

$$\Phi(s) = [\mathrm{f}(t)\,\mathrm{f}(t+s)]_t = \tfrac{1}{2}[\mathrm{Re}\,\{\mathrm{e}^{2i\omega_0 t}\,\mathrm{e}^{i\omega_0 s}\,\mathrm{e}^{i[\eta(t+s)+\eta(t)]}\} + \mathrm{Re}\,\{\mathrm{e}^{i\omega_0 s}\,\mathrm{e}^{i[\eta(t+s)-\eta(t)]}\}]_t$$

where $[\ ]_t$ indicates the average value over all values of t. Now the first term in the expression for $\Phi(s)$ is zero provided that no significant disturbance in phase occurs, on the average, within one cycle of oscillation. For optical spectra, where the linewidth is a small fraction of the undisturbed frequency, this is a very good approximation, but it should be noticed that the results obtained with its use cannot be extrapolated to give the correct zero frequency results. For our purposes, then, we may write

$$\begin{aligned}\Phi(s) &= \tfrac{1}{2}\{\mathrm{Re}\,[\mathrm{e}^{i\omega_0 s}\,\mathrm{e}^{i\eta(t,s)}]\}_t\\ &= \tfrac{1}{4}\{\mathrm{e}^{i\omega_0 s}\,[\mathrm{e}^{i\eta(t,s)}]_t + \mathrm{e}^{-i\omega_0 s}\,[\mathrm{e}^{-i\eta(t,s)}]_t\}\\ &= \Psi(s) + \Psi^*(s) \qquad (3)\end{aligned}$$

where $\eta(t,s) = \eta(t+s) - \eta(t)$.

Finally we recall that the intensity profile is the complex Fourier transform of the autocorrelation function of the disturbance:

$$I(\omega) = \int_{-\infty}^{+\infty} \Psi(s)\,\mathrm{e}^{i\omega s}\,\mathrm{d}s + \int_{-\infty}^{+\infty} \Psi^*(s)\,\mathrm{e}^{i\omega s}\,\mathrm{d}s. \qquad (4)$$

No further progress can be made without evaluating the time averages, and to accomplish this approximations must be made.

2. *The impact approximation*

We first write down an expression for $\Delta[\Psi(s)\mathrm{e}^{-i\omega_0 s}]$, a change, not necessarily small, in $\Psi(s)\mathrm{e}^{-i\omega_0 s}$ corresponding to a change Δs in s:

$$\begin{aligned}\Delta[\Psi(s)\mathrm{e}^{-i\omega_0 s}] &= \tfrac{1}{2}[\mathrm{e}^{i\eta(t,s)}\,(\mathrm{e}^{i\Delta\eta} - 1)]_t\\ &= \tfrac{1}{2}[\mathrm{e}^{i\eta(t,s)}]_t\,[\mathrm{e}^{i\Delta\eta} - 1]_t\\ &= \Psi(s)\mathrm{e}^{-i\omega_0 s}\,[\mathrm{e}^{i\Delta\eta} - 1]_t\end{aligned}$$

where $\Delta\eta = \eta(t,s+\Delta s) - \eta(t,s)$

and the second line follows because the changes $\Delta\eta$ occurring in an oscillator perturbed by random collisions are statistically independent of η, the accumulated phase disturbance at time s. We next suppose that the phase changes $\Delta\eta$ are caused by successive collisions. This is known as the impact approximation and its range of validity will be discussed later in this section. The number of collisions with impact parameter ρ which occur in the time interval Δs is $N\bar{v}\,2\pi\rho\mathrm{d}\rho|\Delta s|$ where

N is the number density of perturbing particles and the further assumption has been made that the perturbing and radiating atoms move in straight lines with mean relative velocity $\bar{v}$. We then have

$$[\mathrm{e}^{i\Delta\eta} - 1]_t = 2\pi N\bar{v}|\,\Delta s\,|\int_0^\infty [\mathrm{e}^{i\eta(\rho)} - 1]\,\rho\,\mathrm{d}\rho$$

where $\eta(\rho)$ is the phase change caused by a collision of impact parameter ρ. We write the integral in the form

$$[\mathrm{e}^{i\Delta\eta} - 1]_t = -\,N\bar{v}|\,\Delta s\,|\,(\sigma_r - i\sigma_i)$$

where

$$\sigma_r = 2\pi\int_0^\infty [1 - \cos\eta(\rho)]\,\rho\,\mathrm{d}\rho \tag{5}$$

and

$$\sigma_i = 2\pi\int_0^\infty \sin\eta\,(\rho)\,\rho\,\mathrm{d}\rho. \tag{6}$$

It follows that

$$\frac{\Delta[\Psi(s)\mathrm{e}^{-i\omega_0 s}]}{\Psi(s)\mathrm{e}^{-i\omega_0 s}} = -\,N\bar{v}|\,\Delta s\,|\,(\sigma_r - i\sigma_i).$$

Since the average over a large number of collisions is involved, this last expression can be treated as a differential equation. Integration then gives

$$\Psi(s) = \text{constant} \times \exp\,\{[i\omega_0 - N\bar{v}\,(\sigma_r - i\sigma_i)]|\,s\,|\}. \tag{7}$$

Thus the spectrum is, from eqns. (4) and (7),

$$I(\omega) = 2N\bar{v}\sigma_r\left\{\frac{1}{(\omega_0 + \omega + N\bar{v}\sigma_i)^2 + (N\bar{v}\sigma_r)^2} + \frac{1}{(\omega_0 - \omega + N\bar{v}\sigma_i)^2 + (N\bar{v}\sigma_r)^2}\right\}. \tag{8}$$

In optical spectra the first of the two terms in the final expression for $I(\omega)$ is negligible compared with the second. Neglecting the first term, and normalizing so that

$$\int_0^\infty I(\omega)\, \mathrm{d}\omega = 1,$$

we obtain

$$I(\omega) = \frac{N\bar{v}\sigma_r/\pi}{(\omega_0 - \omega + N\bar{v}\sigma_i)^2 + (N\bar{v}\sigma_r)^2}. \tag{9}$$

The spectral line therefore has a Lorentzian shape, but the whole line is shifted with respect to the undisturbed line centre at ω_0. It is clear that the quantity $\sigma_r - i\sigma_i$ can be looked on as a complex cross-section, and that the broadening of the line is associated with the real part σ_r of this cross-section and the shift with the imaginary part $-\sigma_i$. It is also easy to see from eqns. (5) and (6) that, since $\eta(\rho)$ increases rapidly as ρ decreases, the contribution to σ_i arises predominantly from small values of η while that to σ_r arises predominantly from large values of η. This corresponds to the original physical idea of Weisskopf (1933) that the broadening arises essentially for collisions which cause a phase change greater than about 1 radian.

All that remains to press this classical calculation to a numerical conclusion is to evaluate $\eta(\rho)$ and then perform the integrations in eqns. (5) and (6). If the interatomic potentials of the upper and lower states of the radiating atom and the perturbing atom (taken to be in the ground state) are respectively $V_u(R)$ and $V_l(R)$, where R is the distance between the two atoms, then

$$\eta(\rho) = \frac{1}{\hbar}\int_{-\infty}^{+\infty} [V_u(R) - V_l(R)]\, \mathrm{d}t = \frac{1}{\hbar}\int_{-\infty}^{+\infty} V(R)\, \mathrm{d}t$$

where t represents the time measured from the time of closest approach of the colliding atoms. If we assume that the atoms move in straight paths with velocity $\bar{v}$, then,

$$R^2 = \rho^2 + \bar{v}^2 t^2$$

so that

$$\eta(\rho) = \frac{2}{\bar{v}\hbar} \int_0^\infty \frac{V(R)R\mathrm{d}R}{(R^2 - \rho^2)^{1/2}}. \tag{10}$$

The question of a suitable form for the functions $V(R)$ will be taken up in section 2C.

We now turn to an examination of the validity of the important approximations which have been made.

First we consider the impact approximation itself. Although much has been written about this (see the reviews mentioned in the Introduction), the essential idea is very simple. The collisions are supposed to occur successively and to occupy a time small compared with the time between collisions. The radiation emitted during the collisions may then be neglected. Now the duration of a collision is $\tau_c \sim \rho/\bar{v}$ and the mean time between collisions which cause broadening is $\bar{\tau} = (N\bar{v}\sigma_c)^{-1}$. We compare the intensity per unit frequency interval from τ_c with that from $\bar{\tau}$ at a given frequency displacement $(\omega_0 - \omega)$ from the line centre. Remembering that the former contribution is spread over an interval $\sim\tau_c^{-1}$, the ratio of the two contributions is approximately

$$\frac{(\rho/\bar{v})^2}{(N\bar{v}\sigma_r)^{-1}} \frac{\pi(\omega_0 - \omega)^2}{N\bar{v}\sigma_r} = \frac{\pi\rho^2(\omega_0 - \omega)^2}{\bar{v}^2}.$$

If the impact approximation is to be valid this ratio must be $\ll 1$. Hence

$$(\omega_0 - \omega)^2 \ll \bar{v}^2/\pi\rho^2. \tag{11}$$

But the value of $\omega_0 - \omega$ associated with a certain value of ρ is determined by the interatomic potential. We put

$$\omega_0 - \omega = - V(\rho)/\hbar$$

and write the solution of this equation as

$$\rho = W(\omega_0 - \omega).$$

The inequality which defines the region of validity of the impact approximation may then be written

$$(\omega_0 - \omega)^2 W^2 \ll \bar{v}^2/\pi.$$

If $|V(\rho)|$ is a single-valued function of ρ which decreases more rapidly than linearly with ρ, then $(\omega_0 - \omega)^2 W$ is an increasing function of $|\omega_0 - \omega|$. The impact approximation is therefore seen to be valid at small frequency displacements and to be essentially a high velocity approximation. If $V(\rho)$ is not a single-valued function, and in practice it never is (but has the characteristic shape of an interatomic potential), the impact region is more difficult to define. But in most cases, the general conclusion already mentioned is valid. If we take the van der Waals interaction, $V(\rho) = -C_6/\rho^6$, giving $W(\omega_0 - \omega) = (C_6/\hbar)^{1/6}/(\omega_0 - \omega)^{1/6}$, the inequality (5) becomes

$$|\omega_0 - \omega| \leqslant \left(\frac{\bar{v}}{\sqrt{\pi}}\right)^{6/5} \left(\frac{\hbar}{C_6}\right)^{1/5}. \tag{12}$$

For neutral atom pairs $C_6 \sim 10^{-57}$ erg cm^6, and for many experiments $\bar{v} \sim 10^5$ cm sec^{-1}. With these values, we find the impact region defined as

$$|\omega_0 - \omega| \leqslant 3 \times 10^{11} \text{ rad sec}^{-1} = 1.5 \text{ cm}^{-1}.$$

Although values of C_6 and $\bar{v}$ can, of course, vary over a certain range, the impact region is mostly defined by a boundary of a few wavenumbers. It is of some consequence to notice that this boundary occurs on one wing only of the line. If C_6 is positive (the usual case), then $\omega_0 - \omega$ is positive and the boundary refers to the low frequency wing of the line. If the potential is entirely described by the van der Waals interaction, the impact approximation is, according to the above account, valid for all positions on the high frequency wing of the line: all radiation emitted during the collisions is displaced to longer wavelengths. In fact, for very close encounters the "repulsive" part of the potential curve causes radiation to be emitted on the high frequency side of the line centre, so that in practice an impact boundary arises on that side also. Taking the Lennard-Jones form $V(\rho) = C_{12}/\rho^{12} - C_6/\rho^6$ it turns out, with typical values for the constants, that the impact boundary on the low frequency side is not usually affected by the presence of the R^{-12} term, and that on the high frequency side the boundary is determined only by the repulsive term. With $C_{12} = 10^{-104}$ erg cm^{12} and $\bar{v} = 10^5$ cm sec^{-1}, we find

$$|\omega_0 - \omega| \leqslant 3 \times 10^{12} \text{ rad sec}^{-1} = 15 \text{ cm}^{-1}.$$

Secondly we examine the validity of the assumption that the atoms move in straight lines. A qualitative calculation can be made to estimate the range of applicability of the straight path approximation.

The orbit will be significantly curved if the impulse of the force F exerted between the colliding atoms becomes comparable with the momentum of either of them. The relevant ratio is therefore

$$p = \frac{\int F \mathrm{d}t}{M\bar{v}} \sim -\frac{(\mathrm{d}V/\mathrm{d}R)_{R=\rho}}{M\bar{v}} \frac{\rho}{\bar{v}} = \frac{6}{M\bar{v}^2}\left[\frac{2C_{12}}{\rho^{12}} - \frac{C_6}{\rho^6}\right]$$

where M is the mass of the smaller atom involved. Now the phase change, calculated for straight paths, for a Lennard-Jones potential is (Hindmarsh, Petford and Smith, 1967)

$$\eta = \frac{63\pi}{256}\frac{1}{\hbar\bar{v}}\frac{C_{12}}{\rho^{11}} - \frac{3\pi}{8}\frac{1}{\hbar\bar{v}}\frac{C_6}{\rho^5}. \tag{13}$$

If, at the critical value ρ_c of ρ, η is determined essentially by the second term, then p is also so determined. We then have, since $\eta = 1$ at ρ_c,

$$\rho_c{}^5 \sim C_6/\hbar\bar{v}$$

and

$$p \sim \frac{6\hbar}{M\bar{v}\rho_c} = \frac{6\hbar^{6/5}}{M\bar{v}^{4/5}\, C_6{}^{1/5}} \approx 0.1$$

on substituting typical values. Path curvature is therefore small. If C_6 is small, ρ_c is essentially determined by the R^{-12} term. In this case we find $p \sim 1$ with $C_{12} = 10^{-112}$ J cm^{12}. We therefore expect path curvature to have a marked effect. A fundamental point which arises here is how to combine the potentials for the two levels of the radiator which are involved in the transition, since the classical path will not be the same for both levels. This has been discussed by Fiutak and Czuchaj (1970) who point out that the condition $p \ll 1$ for straight paths is essentially the same as the condition for the pertuber motion to be described classically at all (see section 2B 1). Although Schuller and Vodar (1960) have calculated the effect of curvature of the orbits for a Sutherland type of potential, and find significant effects in certain circumstances, a greater effort is probably not worth while unless a full quantum mechanical treatment is used.

Thirdly we mention the problem of velocity averaging. In most of the literature velocity averaging is achieved by the simple device of writing $\bar{v}$, the mean thermal relative speed of the radiating and perturbing atoms wherever the velocity enters the calculation. This is clearly not correct. It is a relatively simple matter to average the phase shift expressions over a Maxwellian velocity distribution, and this in fact makes only a small difference to the numerical results. The real difficulty is that if rigorously correct velocity averaging is to be carried out, the thermal (Doppler) broadening of the spectral line cannot be treated separately from the collision broadening as is usually done. This question has been studied by Gerston and Foley (1968), who refer to the earlier work of Dicke (1953) and Wittke and Dicke (1956) on "pressure narrowing". The essential point is that if the mean free path of the radiating atoms for collisions which change their direction becomes much smaller than the wavelength of the radiation, the Doppler shift induced in one portion of a cycle of the radiation tends to cancel the shift from another portion. The effective Doppler width is then much reduced, and provided the ordinary collision broadening is not too great, a net narrowing with increasing pressure can occur over a certain pressure range. This is not usually the case in optical spectra, but at much lower frequencies the phenomenon is well known.

3. *The quasi-static approximation*

The quasi-static approximation takes into account radiation emitted at all times, but does not make a Fourier analysis. The intensity at an angular frequency ω is thus proportional to the fraction of the total time which the atom spends in radiating at that frequency. If the instantaneous frequency is represented by $\omega = \omega_0 + \Delta\omega$ then the quasi-static theory gives

$$I(\Delta\omega) \propto P(\Delta\omega)$$

where $P(\Delta\omega)$ is the probability of occurrence of the frequency displacement $\Delta\omega$. We now see how this follows from the general theory already outlined. We begin once again with the autocorrelation function $\Phi(s)$ of the disturbance and work as before with the function $\Psi(s)$ defined by

$$\Phi(s) = \Psi(s) + \Psi^*(s).$$

Then

$$\Psi(s) = [\mathrm{e}^{i\omega_0 s}\,\mathrm{e}^{i\eta(t,s)}]_t.$$

The essence of the quasi-static approximation is to assume that $\eta(t,s)$ is a slowly varying function of s, so that in the time that $\eta(t,s)$ has changed significantly, $\mathrm{e}^{i\omega_0 s}$ has undergone a large number of oscillations. We then expand $\eta(t,s)$ in a Taylor series about t:

$$\eta(t,s) = \eta(t+s) - \eta(t) = \frac{\mathrm{d}\eta}{\mathrm{d}t}\,s + \ldots = s\Delta\omega + \ldots$$

since $\Delta\omega = \mathrm{d}\eta/\mathrm{d}t$.

Neglecting all but the first term in the expansion, we have

$$\Psi(s) = \mathrm{e}^{i\omega_0 s}[\mathrm{e}^{is\Delta\omega}]_t.$$

If, then, $P(\Delta\omega)$ is the probability of occurrence of $\Delta\omega$, we may write

$$\Psi(s) = \int_{-\infty}^{+\infty} \mathrm{e}^{i\omega_0 s}\,\mathrm{e}^{is\Delta\omega}\,P(\Delta\omega)\,\mathrm{d}\Delta\omega$$

and the line profile is

$$I(\omega) = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \mathrm{e}^{i(\omega+\omega_0)s}\,\mathrm{e}^{is\Delta\omega}\,P(\Delta\omega)\,\mathrm{d}(\Delta\omega)\,\mathrm{d}s$$

$$+ \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \mathrm{e}^{i(\omega-\omega_0)s}\,\mathrm{e}^{-is\Delta\omega}\,P(\Delta\omega)\,\mathrm{d}(\Delta\omega)\,\mathrm{d}s.$$

Because in the quasi-static approximation the variation in $\Delta\omega$ is slow compared with the oscillations in the integrand, the contribution to the integrals arises solely from the region where the exponent is zero.

It follows immediately that

$$I(\Delta\omega) \propto P(\Delta\omega)$$

as given by the simple argument above.

We now wish to evaluate the occurrence probability $P(\Delta\omega)$ in terms of the interatomic potential. This type of calculation was first performed by Holtsmark (1919) for the special case of broadening by charged particles (where the interaction is either the linear or the quadratic Stark effect) and by Margenau (1932) for the general case of scalarly additive interactions. We assume scalar additivity throughout this article for neutral atom interaction in absence of any knowledge of their non-additivity (apart from calculations with three interacting atoms by Dalgarno and Victor (1967)).

Let us imagine a total of N_T perturbers in a spherical vessel of radius R_0, centred about the radiating atom. The probability of finding a perturber in the spherical shell defined by R and $R + \mathrm{d}R$ is $4\pi R^2 \mathrm{d}R 3N_T/(4\pi R_0^3) = 3N_T R^2 \mathrm{d}R/R_0^3$. Thus we have that

$$P(\Delta\omega) \propto \prod_i \left(\frac{3}{R_0^3}\int_{\Delta\omega} R_i^2 \,\mathrm{d}R_i\right) \tag{14}$$

where R_i is the position of ith perturber, and the integration is over these positions of configuration space which yield the correct perturbation $\Delta\omega$. The integral can, however, be written in such a form that it goes over all space with the use of a Dirichlet factor

$$\int_{-\infty}^{+\infty} \frac{\sin\,(x\,\mathrm{d}(\Delta\omega))}{x}\,\mathrm{e}^{i\Omega x}\,\mathrm{d}x$$

where $\Omega = \dfrac{1}{\hbar}\sum_{i=1}^{N_T} V(R_i) - \Delta\omega$. This factor takes the value π when $\Omega = 0$, i.e. when the total frequency displacement is $\Delta\omega$, and is zero elsewhere; scalar additivity has been assumed at this point. We may therefore write

$$P(\Delta\omega)\,\mathrm{d}(\Delta\omega) = \left(\frac{3}{R_0^3}\right)^{N_T} \int\limits_0^{R_0} \cdots \int\limits_0^{R_0} R_1^2\, R_2^2 \ldots R_{N_T}^2\, \mathrm{d}R_1\, \mathrm{d}R_2 \ldots \mathrm{d}R_{N_T} \int\limits_{-\infty}^{+\infty} \frac{\sin(x\ \mathrm{d}(\Delta\omega))}{x}\, \mathrm{e}^{i\Omega x}\, \mathrm{d}x$$

$$= \left(\frac{3}{R_0^3}\right)^{N_T} \mathrm{d}(\Delta\omega) \int\limits_{-\infty}^{+\infty} \left\{ \int\limits_0^{R_0} R^2\ \mathrm{d}R\ \mathrm{e}^{iV(R)x/\hbar} \right\}^{N_T} \mathrm{e}^{-ix\Delta\omega}\, \mathrm{d}x.$$

It is convenient to introduce the function

$$U(x) = \int\limits_0^{R_0} (1 - \mathrm{e}^{iV(R)x/\hbar})\, R^2\, \mathrm{d}R \tag{15}$$

in which case we have

$$P(\Delta\omega) = \int\limits_{-\infty}^{+\infty} (1 - 3U(x)/R_0^3)^{N_T}\, \mathrm{e}^{-ix\Delta\omega}\, \mathrm{d}x. \tag{16}$$

Next we allow N_T and R_0 to tend to infinity, with the condition that $N_T/\frac{4}{3}\pi R_0{}^3 = N$. This is readily achieved by means of the expression

$$\underset{N_T\to\infty}{\mathrm{Lt}} (1 - 3U(x)/R_0^3)^{N_T} = \underset{N_T\to\infty}{\mathrm{Lt}} (1 - 4\pi U(x)N/N_T)^{N_T} = \mathrm{e}^{-4\pi U(x)N}.$$

We therefore have

$$P(\Delta\omega) = \int\limits_{-\infty}^{+\infty} \mathrm{e}^{-4\pi U(x)N}\, \mathrm{e}^{-ix\Delta\omega}\, \mathrm{d}x.$$

The integral may be expressed in a more convenient form by writing

$$4\pi U(x)N = A(x) + iB(x). \tag{17}$$

Then, recalling that $U(-x) = U^*(x)$, we obtain

$$I(\Delta\omega) \propto P(\Delta\omega) = \int_0^\infty \mathrm{e}^{-A(x)} \cos\{B(x) + x\Delta\omega\}\,\mathrm{d}x. \tag{18}$$

Further progress depends on introducing an explicit form for the interatomic potential $V(R)$, and this will be discussed in section 2C.

B. Quantum Theory of Collision Broadening

1. *General formulation*

We turn now to an exposition of the quantum theory of collision broadening. It is important at the outset to understand the essential differences between the classical and quantum treatments of the problem. We consider quantum effects in the perturbing and radiating atoms separately. The interaction between them is already in effect treated quantum mechanically in the classical theory, for $V(R)$ can be the result of a quantum calculation, provided both states of the radiator can be considered stationary on the time scale of a collision.

The first step is to examine whether the path of a perturber relative to a radiator can be adequately described by a classical orbit. The relevant parameter here is the ratio of the de Broglie wavelength of the atom to the minimum interatomic distance. This latter quantity is defined simply by the impact parameter for the critical "Weisskopf" phase change. Closer collisions, of course, occur, but since they cause larger than critical phase changes in the radiation, the exact phase change and the details of the collision have no effect on the line profile. The condition for the classical path approximation to be valid for most collisions is, then,

$$\frac{h}{m\bar{v}} \ll \rho_c \quad \text{or} \quad \frac{h}{(3mkT)^{\frac{1}{2}}} \ll \rho_c.$$

(As we have already pointed out, this is also the condition which ensures that the path is straight.) Taking the worst case, we have to deal with experiments at a temperature of, say, 20 K with helium as the perturber. For this case the condition becomes

$$\rho_c \gg 3\text{Å}.$$

It is quite possible for this condition not to be very well satisfied, although most experiments are carried out at temperatures of several hundred Kelvin, in which case no difficulty arises. For complete generality, however, the quantum description of the collision orbits must be used.

Secondly, the question arises whether the use of the classical electron oscillator rather than a real atom to describe the emission or absorption of radiation is satisfactory. It is well known that this simple classical atom corresponds closely to a real atom with only two energy levels, or where the two energy levels involved in the transition concerned are completely uncoupled from all other levels. Except where there is degeneracy, or, what amounts to the same thing, where the collision itself causes transitions between energy levels of the radiator, we expect this approximation to be very good. Two kinds of degeneracy are concerned: one is the universal degeneracy associated with the quantum number m, and the other the much rarer accidental degeneracy where levels with different values of other quantum numbers have the same, or nearly the same, energy. If collision induced transitions occur, we expect that not only will the damping constant of the line be changed, but also the shape will no longer be Lorentzian. This is clear from the classical analogue, in which the collisions cause coupling between the oscillation concerned and other modes of oscillation of the system.

The quantum mechanical analogue of eqn. (2) is

$$I(\omega) = \sum_{if} \delta(\omega - \omega_{if}) \, |\langle f \mid \boldsymbol{d} \mid i \rangle|^2 \, \rho_i \tag{19}$$

where the initial and final states $|i\rangle$ and $|f\rangle$ are the time-dependent state functions referring to the whole system of radiators and perturbers. $\delta(\omega - \omega_{if})$ is the Dirac δ-function, which takes the value 1 when $\omega = \omega_{if}$ and is zero elsewhere; ρ_i is the number density of radiators in the state $|i\rangle$, and $\boldsymbol{d}$ the electric dipole moment. As in the case of classical theory, it is easier to calculate the autocorrelation function $\Phi(s)$. Formally, we can write,

$$\Phi(s) = \int_{-\infty}^{+\infty} I(\omega)\, \mathrm{e}^{-i\omega s}\, \mathrm{d}\omega = \sum_{if} \mathrm{e}^{-i\omega_{if}s} \,|\, \langle f \,|\, \boldsymbol{d} \,|\, i \rangle \,|^2\, \rho_i. \tag{20}$$

It is convenient to introduce the time development operator, defined by

$$\mathrm{T}(t) = \mathrm{e}^{-i\mathrm{H}t/\hbar} \tag{21}$$

where H is the time-dependent Hamiltonian operator for the whole system. When $\mathrm{T}(t)$ acts on an eigenstate $|a\rangle$ of H we have

$$\mathrm{T}(t) \,|\, a \rangle = \mathrm{e}^{-iE_a t/\hbar} \,|\, a \rangle$$

where E_a is the eigenvalue of H associated with the state $|a\rangle$. The autocorrelation function may therefore be written in the form

$$\Phi(s) = \sum_{if} \langle f \,|\, \boldsymbol{d}\, \mathrm{T}(s) \,|\, i \rangle \langle i \,|\, \boldsymbol{d}\, \mathrm{T}^*(s) \,|\, f \rangle\, \rho_i \tag{22}$$

where the asterisk on an operator means Hermitian conjugate.

No further progress can be made without introducing $|i\rangle$ and $|f\rangle$ explicitly. At this point we abandon a wholly general treatment, and invoke the classical path approximation. We refer to the article by Baranger (1962) for an account of the complete quantum mechanical theory: to our knowledge it has never been used in the interpretation of measurements of collision broadening by neutral perturbers.

2. *The classical path approximation*

We begin by writing the Hamiltonian for the complete system as

$$\mathrm{H} = \mathrm{H}_A + \mathrm{H}_P + \mathrm{V}$$

where H_A, H_P and V are respectively the Hamiltonians for the radiating atom, the perturbers and the interaction between the radiator and perturbers, and the wavefunction for the system as

$$\psi(t) = \chi(t)\phi(t) \tag{23}$$

where $\chi(t)$ and $\phi(t)$ are respectively the time-dependent wave functions for the radiator and the perturbers; $\chi(t)$ depends on the coordinates of the radiator only and $\phi(t)$ on those of the perturbers only. This wave function ignores the interaction between radiator and perturbers, and this influence must be evaluated by perturbation theory. The wave function describing the motion of the perturbers obeys the time dependent Schrödinger equation:

$$i\hbar \frac{\mathrm{d}\phi(t)}{\mathrm{d}t} = \mathrm{H}_p\, \phi(t).$$

To find the equation obeyed by $\chi(t)$, we multiply eqn. (23) by $\phi^*(t)$ and integrate over the perturber coordinates χ_p:

$$\chi(t) = \int \psi(t)\, \phi^*(t) \mathrm{d}x_p,$$

from which we obtain

$$\hbar \frac{\mathrm{d}\chi(t)}{\mathrm{d}t} = -\int \psi(t)\, \mathrm{H}_p\, \phi^*(t)\, \mathrm{d}x_p + \int (\mathrm{H}_A + \mathrm{H}_p + \mathrm{V})\, \psi(t)\, \phi^*(t)\, \mathrm{d}x_p$$
$$= [\mathrm{H}_A + \mathrm{v}(t)]\chi(t) \tag{24}$$

where

$$\mathrm{v}(t) = \int \phi^*(t)\, \mathrm{V}\, \phi(t)\, \mathrm{d}x_p. \tag{25}$$

We can therefore proceed as though the atomic wave function $\chi(t)$ is subject to a time varying perturbation given by $\mathrm{v}(t)$, and in the classical path approximation (that is with the $\phi(t)$ assumed to be localized wave packets) $\mathrm{v}(t)$ is given simply by the classical potential describing the rapidly varying interaction between the radiator and perturbers.

The effect of the perturbers may then be taken into account by writing a time development operator T_A which operates on the perturbed atomic wave function $\chi(t)$ and is defined by

$$i\hbar \frac{\mathrm{d}\mathrm{T}_A(t)}{\mathrm{d}t} = [\mathrm{H}_A + \mathrm{v}(t)]\, \mathrm{T}_A(t).$$

The autocorrelation function $\Phi(s)$ now becomes

$$\Phi(s) = \sum_{a\alpha} [\langle a \mid \boldsymbol{d}\, \mathrm{T}_A(t,s) \mid \alpha \rangle \langle \alpha \mid \boldsymbol{d}\, \mathrm{T}_A^*(t,s) \mid a \rangle + \text{c.c.}]_t \quad (26)$$

where $\mathrm{T}_A(t,s) = \mathrm{T}_A(t+s) - \mathrm{T}_A(t)$, a labels the upper states and α the lower states of the atomic transition, the average is taken over all times t and c.c. stands for complex conjugate. To clarify the analogy with the classical expression, we separate the time dependent from the time independent factors, and write $\Phi(s)$ in the expanded form:

$$\Phi(s) = \sum_{ab\alpha\beta} [\langle a \mid \boldsymbol{d} \mid \alpha \rangle \langle \beta \mid \boldsymbol{d} \mid b \rangle \langle b \mid \mathrm{T}_A(t,s) \mid a \rangle \langle \alpha \mid \mathrm{T}_A^*(t,s) \mid \beta \rangle + \text{c.c.}]_t \quad (27)$$

If there is only a single upper state $|a\rangle$ and a single lower state $|\alpha\rangle$ involved there is only one term in the summation and (27) reduces to

$$\Phi(s) = |\langle a \mid \boldsymbol{d} \mid \alpha \rangle|^2 [\langle \alpha \mid \mathrm{T}_A^*(t,s) \mid \alpha \rangle \langle a \mid \mathrm{T}_A(t,s) \mid a \rangle + \text{c.c.}]_t \quad (28)$$

which, apart from a numerical factor, is equivalent to eqn. (3).

It is convenient for further development to work with the time evolution operator in an interaction representation. We write

$$\mathrm{U}(0,s) = \exp(i\mathrm{H}_A s/\hbar)\, \mathrm{T}(0,s).$$

This is precisely analogous to the device of working with $\Psi(s)e^{-i\omega_0 s}$ in the classical treatment. We then have

$$i\hbar \frac{\mathrm{dU}}{\mathrm{d}s} = \exp\,(i\mathrm{H}_A s/\hbar)\mathrm{v}(t)\exp(-\,i\mathrm{H}_A s/\hbar)\mathrm{U} = \mathrm{v}'(t)\mathrm{U}$$

This equation may be solved by the standard perturbation expansion:

$$\mathrm{U}(0,s) = 1 - (i/\hbar)\int_0^s \mathrm{v}'(s_1)\,\mathrm{d}s_1 + (i/\hbar)^2 \int_0^s \mathrm{v}'(s_1)\,\mathrm{d}s_1 \int_0^{s_1} \mathrm{v}'(s_2)\,\mathrm{d}s_2 + \ldots$$

while in terms of U(s) the correlation function becomes

$$\Phi(s) = \sum_{ab\alpha\beta} [\langle a \mid \boldsymbol{d} \mid \alpha \rangle \langle \beta \mid \boldsymbol{d} \mid b \rangle \mathrm{e}^{i(E_\beta - E_b)t/\hbar}$$

$$\langle \alpha \mid \mathrm{U}^*(t,s) \mid \beta \rangle \langle b/\mathrm{U}(t,s) \mid a \rangle + \mathrm{c.c.}]_t \tag{29}$$

3. *The impact approximation*

The calculation of the average in the impact approximation now follows very closely the classical calculation of section 2A 2. The change $\Delta\Phi(s)$ in $\Phi(s)$ is written down; it involves $\Delta[\mathrm{U}(t,s)]_t$ which is evaluated with the use of the impact approximation, namely that the two factors in $\Delta[\mathrm{U}(t,s)]_t = [\mathrm{U}(t,s)(\mathrm{U}(t,s + \Delta s) - 1)]_t$ are statistically independent, and that the phase changes are caused by successive collisions. Just as in the classical case the line profile is Lorentzian provided there is no overlapping of lines, and the damping constant and shift are given by

$$\gamma = 2\pi N\bar{v} \int_0^\infty \{1 - \mathrm{e}^{-\mu_i - \mu_f} \cos(\eta_i - \eta_f)\} \rho \mathrm{d}\rho \tag{30}$$

$$\beta = 2\pi N\bar{v} \int_0^\infty \mathrm{e}^{-\mu_i - \mu_f} \sin(\eta_i - \eta_f) \rho \mathrm{d}\rho \tag{31}$$

where

$$\mathrm{e}^{-\mu_i - i\eta_i} = \langle a \mid S \mid a \rangle \tag{32a}$$

$$\mathrm{e}^{-\mu_f - i\eta_f} = \langle \alpha \mid S \mid \alpha \rangle \tag{32b}$$

and

$$S = 1 - (i/\hbar) \int_{-\infty}^{+\infty} \mathrm{v}'(s_1)\, \mathrm{d}s_1 + (i/\hbar)^2 \int_{-\infty}^{+\infty} \mathrm{v}'(s_1)\, \mathrm{d}s_1 \int_{-\infty}^{+\infty} \mathrm{v}'(s_2)\, \mathrm{d}s_2 + \ldots \tag{33}$$

is the perturbation expansion of the S-matrix, defined by

$$S = \mathrm{U}(\infty, -\infty)$$

In these expressions, μ represents inelastic and η elastic (phase changing) collisions. If the inelastic collisions are ignored, $\mu = 0$, and the expressions for γ and β reduce to those obtained with the use of classical theory. In this case the phase changes can be calculated without resort to perturbation theory.

The neglect of inelastic collisions is certainly justifiable for foreign gas broadening where the energy levels of the radiating atom are so far separated that the frequencies present in the collision, of the order of the reciprocal of the duration of the collision, are smaller than those which correspond to the energy-level separations. Schuller and Oksengorn (1969b) have investigated the case of the alkali atoms with their fine structure doublets, but have concluded that the inelastic collisions cause a significant contribution to the broadening and shift only in the case of lithium. The fundamental reason for this is that, although the cross-section for inelastic collisions is quite large for transitions between certain fine structure components, it is, except for lithium, significantly smaller than that for phase changes of order unity (i.e. the Weisskopf cross-section).

The case of self-broadening is quite different. Here the essence of the process is the exchange of the energy of excitation between the radiator and the perturber, and inelastic effects are all-important. A number of quantum mechanical calculations have been performed, the results of which are quoted in section 3B 2.

The question of the effect of degeneracy with respect to the quantum number m requires some further comment. It arises even in the classical theory, where it takes the form of enquiring whether the radiating oscillator rotates through an angle π as the perturber flies past. If this always occurred, the result of every collision would be a phase change in the radiation of at least π. Experimental evidence clearly rules this out, and it has usually been assumed that no rotation occurs for collisions which would otherwise produce phase changes of less than about unity. In quantum theory the question is raised by asking whether, in the laboratory coordinate system, the m-value of the radiator changes as a result of a collision. According to Baranger (1962), if the atomic

Hamiltonian H_A is invariant under rotations and if the collisions occur isotropically, the question can be evaded, and the averaging over m carried out in a way which, in fact, amounts to what is usually done in classical theory: the interaction potential is simply averaged over m. The difficulty is, however, that this seems to assume that, in the coordinate system defined by the collision axis, a large number of transitions between the several m-states takes place, and the question must be raised as to whether this is really so. The whole matter seems to be rather obscure, and further clarification is needed.

If the collision broadened lines of a spectrum overlap, eqns. (30) and (31) for γ and β are no longer valid. Off-diagonal elements of the S-matrix need to be calculated, and the matrix for the whole system of overlapping levels diagonalized. The line profiles are not Lorentzian, nor in general are they simply the sum of the Lorentzian profiles of each component in the overlapping system. Little detailed experimental or theoretical investigation of such cases has been carried out for neutral atom broadening; much more has been done for broadening by charged particles, but this falls outside the scope of this review.

C. Interatomic Potential

1. *Introduction*

The theory of collision broadening has been described in sections 2A and 2B without reference to any specific interaction. We must now direct our attention to the choice of a suitable model for the interatomic potential. In the following paragraphs we make initially some general remarks about the interaction between pairs of atoms, both like and unlike, and then go on to describe the predictions of collision-broadening theory in its various approximations when different potentials are assumed.

It was London (1930) who first evaluated by a quantum mechanical method, the long-range, attractive, van der Waals part of the potential between neutral atoms: the well-known dispersion contribution. He wrote the classical electrostatic interaction between two neutral atoms in a series expansion in R^{-1} (where R is the internuclear distance) and treated this as a perturbation on the system. Since the results of this calculation are rather different when the atoms are like and unlike, we shall treat the two cases separately.

When the two atoms are unlike (as in foreign-gas broadening) London's calculation shows that the first-order perturbation energy is zero, but that there is a second-order term

$$\Delta E = R^{-6} \frac{3e^4\hbar^4}{2m^2} \sum_{\substack{k \neq k' \\ l \neq l'}} \frac{f_{kk'} f_{ll'}}{(E_{k'} - E_k)(E_{l'} - E_l)(E_{k'} + E_{l'} - E_k - E_l)} \tag{34}$$

where one atom is in state $|k\rangle$, the other in state $|l\rangle$, $f_{kk'}$ is the oscillator strength of transition $k \to k'$ for the first atom, $f_{ll'}$ applies similarly for the second atom, and E_k, E_l are the energies of the states of the two atoms. (There are also higher order dispersion terms in R^{-8}, R^{-10} . . . to which we shall refer below.)

This expression may be greatly simplified if the perturbing atom has a much greater separation of its energy states than the optically active atom (that is, if it has a lower polarizability); this situation is frequently the case in collision-broadening experiments, where the spectral lines are often those of alkali or alkaline-earth elements and the perturbers are often rare-gas atoms. The term $(E_{k'} + E_{l'} - E_k - E_l)$ in the denominator may then be set approximately equal to $(E_{l'} - E_l)$, where l refers to the low-polarizability atom, and the summation separated into two summations, each involving only one atom. This procedure permits the expression of the second-order potential energy in terms of the dipole polarizability α_d of the perturber, and we have

$$\Delta E = -R^{-6} e^2 \alpha_d \sum_{k' \neq k} |\langle k | \boldsymbol{r} | k' \rangle|^2 \tag{35}$$

(see Unsöld, 1955). In the case of a one-electron spectrum, this expression may be further simplified to

$$\Delta E = -R^{-6} e^2 \alpha_d \overline{r_k^2} \tag{36}$$

where $\overline{r_k{}^2}$ is the mean squared radius of the orbit of the optical electron in state $|k\rangle$. A value for $\overline{r_k{}^2}$ which agrees with more sophisticated calculations to within 5%, is found using the formula

$$\overline{r_k{}^2} = \tfrac{1}{2}a_0^2\, n^{*2}\, \{5n^{*2} + 1 - 3l(l+1)\} \tag{37}$$

where a_0 is the radius of the first Bohr orbit, n^* is the effective principal quantum number of the state $|k\rangle$ and l is the orbital angular momentum quantum number. In foreign-gas broadening studies, then, a suitable model for the long range interaction is

$$V(R) = -\, C_6 R^{-6} \tag{38}$$

where in many instances $C_6 = e^2\, \alpha_d\, (\overline{r_u^2} - \overline{r_l^2})$ and the subscripts u and l refer respectively to the upper and lower states of the transition.

At short range, when the wave-functions of the interacting atoms overlap appreciably, a force of repulsion must become the dominant term in the interaction. It is convenient algebraically to assume that the potential in this range varies as R^{-12}, a form which has been used in kinetic theory as well as in the study of collision effects. That is, we write

$$V(R) = +\, C_{12}\, R^{-12}$$

where $C_{12} = C_{12}$ (upper) $- \, C_{12}$ (lower). A semi-empirical method of finding the constant C_{12} was suggested by Hindmarsh (1963), who made the assumption that the repulsive potential between any pair of atoms will be the same when the radial charge density between them has a particular value chosen to give the best fit to the experimental results; that is

$$C_{12} = qR_0^{12}$$

where q is a constant, $R_0 = R_1 + R_2$ and R_1, R_2 are the radii of the atoms 1, 2 where the radial charge density has the appropriate value. Hindmarsh found that using both Coulomb and Hartree–Fock wave-functions, a radial charge density of 0.012 a.u. to define R_1 and R_2 and a value for q of $(0.9 \pm 0.3) \times 10^{-23}$ J gave best agreement with experimental results. The degree of correlation between experiment and this simple theory, shown in Fig. 1, is remarkably good.

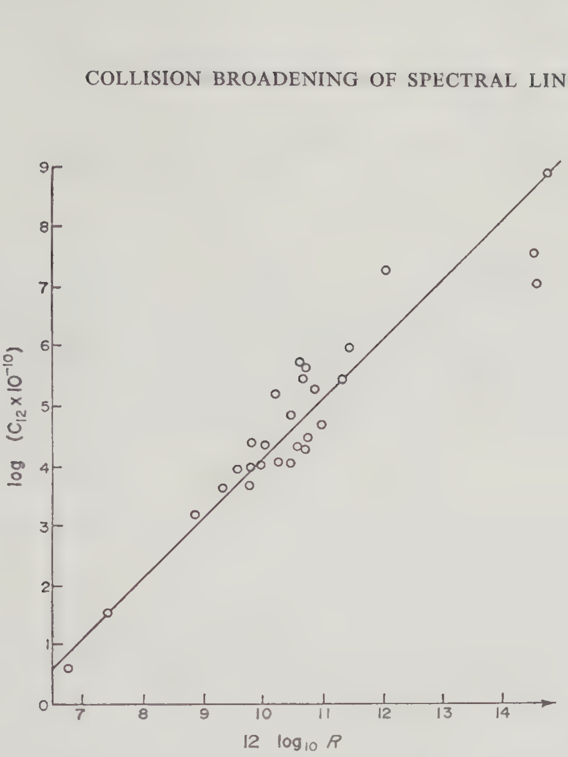

FIG. 1. The correlation in experimental results between C_{12} and R^{12} where R is an internuclear separation defined in the text. R is in Å and C_{12} in erg Å^{12}.

With these considerations in mind, it is clear that the Lennard-Jones (12,6) potential

$$V(R) = C_{12} R^{-12} - C_6 R^{-6} \tag{39}$$

forms a useful model, in terms of which foreign-gas broadening data may be interpreted. Indeed, this potential has been widely used in recent years since it became clear that many observed features could not be interpreted in terms of the single parameter van der Waals potential. The one major difficulty with the Lennard-Jones model has been the discrepancy between theoretical C_6 values and those experimentally derived: the latter generally exceed the former by factors of about 3. The possibility that this discrepancy may be caused by neglect of the higher order dispersion terms in R^{-8}, R^{-10} . . . has been investigated by Hindmarsh, du Plessis and Farr (1970), who used the (12,8,6) potential

$$V(R) = C_{12}\, R^{-12} - C_8\, R^{-8} - C_6\, R^{-6}, \tag{40}$$

and found that the situation was considerably improved in many cases.

Another possible source of difficulty is the assumption of straight trajectories for the colliding atoms. This point has been investigated by Schuller and Vodar (1960a, b), who used classical paths in their calculation, assuming a potential of the form

$$V(R) = \infty,\ R < \sigma,$$

$$V(R) = -\, C_6\, R^{-6},\ R > \sigma.$$

The effects of these refinements, together with the simpler potentials already described, are discussed below.

A knowledge of the interaction between like neutral atoms is required for resonance broadening studies, where "resonance broadening" refers to the broadening of an excited atomic energy level through interaction with like atoms in the ground state, the two levels being linked by a strong dipole transition. (See, for example, Kuhn and Lewis (1969).)

London's perturbation calculation shows that the first-order term is not zero when the interacting atoms are of the same species; in fact, in many cases it is possible to neglect all terms of higher order for the purposes of pressure broadening. This leading term has the value

$$\Delta E = R^{-3}\, \frac{\gamma e^2 \hbar f}{4\pi m \omega_0}$$

where R is the interatomic distance, f and ω_0 are the oscillator strength and angular frequency respectively of the resonance line. The factor γ takes the value -2 if the magnetic quantum number m of the excited atom (relative to the interatomic axis) is 0, and the value $+1$ if $m \pm 1$. Thus sum rules show that positive and negative values of ΔE occur with equal probability. The root mean square value over all m in the J representation has been given by Foley (1946), with the result that the J dependence of ΔE is expressed in the following equation:

$$\Delta E = R^{-3}\, \frac{\sqrt{3} e^2 \hbar f}{8\pi m \omega_0} \left(\frac{2J + 1}{2J' + 1}\right)^{1/2}.$$

A proper understanding of resonance broadening requires quantum mechanical calculations, the results of which are discussed in section 3B 2.

2. *The impact approximation*

With the assumptions of the impact approximation, classical collision-broadening theory, and also quantum theory if collision induced transitions are ignored, shows that the spectral line will always be Lorentzian in shape; the half-intensity width and shift, however, are sensitive to the choice of potential. Recalling the results of the calculations of section 2A 2, we have

$$2\gamma = 2N\bar{v}\sigma_r \tag{41}$$

and

$$\beta = N\bar{v}\sigma_i \tag{42}$$

where σ_r and σ_i are given by eqns. (5) and (6).

How the values of 2γ and β depend on $V(R)$ is examined below.

(i) $V(R) = \pm C_p R^{-p}$. For this general inverse-power potential, integration of eqn. (10) by parts yields the result

$$\eta(\rho) = \pm \pi^{1/2} \frac{\Gamma(p-\frac{1}{2})}{\Gamma(p/2)} \frac{C_p}{\hbar\bar{v}} \rho^{1-p} \tag{43}$$

from which it follows that

$$\sigma_r = \pi^{p/p-1} \left(\frac{C_p}{\hbar\bar{v}}\right)^{2/p-1} \left[\frac{\Gamma(p-\frac{1}{2})}{\Gamma(p/2)}\right]^{2/p-1} \Gamma\left(\frac{p-3}{p-1}\right) \cos\frac{\pi}{p-1} \tag{44}$$

and

$$\sigma_i = \pi^{p/p-1} \left(\frac{C_p}{\hbar\bar{v}}\right)^{2/p-1} \left[\frac{\Gamma(p-\frac{1}{2})}{\Gamma(p/2)}\right]^{2/p-1} \Gamma\left(\frac{p-3}{p-1}\right) \sin\frac{\pi}{p-1} \tag{45}$$

providing that $p > 3$. The sign of σ_r is always positive; the sign of σ_i is the same as that of $V(R)$. Clearly then, the ratio $|\beta/\gamma|$ is $\tan(\pi/p-1)$.

The connection between Weisskopf's simplified treatment, which gives a zero shift, and the more detailed results of the Lindholm–Foley treatment described here, may be understood readily. Weisskopf assumes only strong collisions to be effective (that is, collisions for which $\eta > 1$ radian, and $\rho > \rho_0$, where $\eta(\rho_0) = 1$) and neglects entirely the effect of weak collisions. Now for a strong collision, $\cos \eta(\rho)$ and $\sin \eta(\rho)$ are rapidly oscillating functions which average approximately to zero. Thus, strong collisions give $2\gamma \sim 2\pi N\bar{v}\rho_0^2$ and $\beta \sim 0$. The weak, distant collisions, on the other hand, cause small phase shifts, so that $\cos \eta(\rho) \sim 1$ and $\sin \eta(\rho) \sim \eta(\rho)$; from this it follows that $2\gamma \sim 0$ and $\beta \sim 2\pi N\bar{v}\langle\eta\rangle$, where $\langle\eta\rangle$ is the mean phase shift occurring between two strong collisions. Close collisions, then, cause most of the broadening of the line and the distant collisions are responsible for the shift.

(ii) $V(R) = -C_6R^{-6}$. Substitution of $p = 6$ and the assumption of the negative sign in (i) leads immediately to the expected broadening and shift for a van der Waals potential, so that

$$2\gamma = 8.16\,(C_6/\hbar)^{2/5}\,\bar{v}^{3/5}N$$

and

$$\beta = -\,2.96\,(C_6/\hbar)^{2/5}\,\bar{v}^{3/5}N$$

and the ratio $2\gamma/\beta = -\,2.8$. It was in fact the failure of many observations to produce a ratio in even approximate agreement with this which led some investigators to explore the possibilities of the Lennard-Jones potential.

(iii) $V(R) = C_{12}R^{-12} - C_6R^{-6}$. The Lindholm–Foley theory in the impact approximation was developed for the Lennard-Jones (12, 6) potential by Behmenburg (1964) and independently by Hindmarsh, Petford and Smith (1967). Here we have

$$\eta(\rho) = \frac{63\pi}{256}\frac{C_{12}}{\hbar\bar{v}}\,\rho^{-11} - \frac{3\pi}{8}\frac{C_6}{\hbar\bar{v}}\,\rho^{-5} = \alpha x^{-11} - x^{-5}$$

where

$$x = \rho\left(\frac{3\pi}{8}\frac{C_6}{\hbar\bar{v}}\right)^{-1/5} \tag{46}$$

and

$$\alpha = \frac{63\pi}{256}\left(\frac{8}{3\pi}\right)^{11/5} \bar{v}^{6/5}\, C_{12}\, \hbar^{6/5}/C_6^{11/5} \tag{47}$$

following the notation of Hindmarsh *et al.* Thus,

$$2\gamma = 8\pi\left(\frac{3\pi}{8}\right)^{2/5} N\bar{v}^{3/5}\,(C_6/\hbar)^{2/5}\, B(\alpha) \tag{48}$$

and

$$\beta = 2\pi\left(\frac{3\pi}{8}\right)^{2/5} N\bar{v}^{3/5}(C_6/\hbar)^{2/5}\, S(\alpha) \tag{49}$$

where

$$B(\alpha) = \int_0^\infty x \sin^2\{\tfrac{1}{2}(\alpha x^{-11} - x^{-5})\}\,\mathrm{d}x \tag{50}$$

and

$$S(\alpha) = \int_0^\infty x \sin\,(\alpha x^{-11} - x^{-5})\,\mathrm{d}x \tag{51}$$

The functions $B(\alpha)$ and $S(\alpha)$ are tabulated by these authors for a wide range of values of α; we show them here in graphical form in Fig. 2, along with the function $\frac{1}{2}S(\alpha)/B(\alpha)$, which is the ratio β/γ. In order to interpret experimental results in terms of a (12, 6) potential, this latter curve is used with the experimental ratio to determine α, and hence $S(\alpha)$ and $B(\alpha)$. Then, with the use of either of the measured values β/N or γ/N, C_6 and C_{12} are found by a straightforward calculation. Unfortunately, the oscillatory character of the functions S and B sometimes leads to ambiguous results, although it is often possible to deduce the appropriate pair of constants.

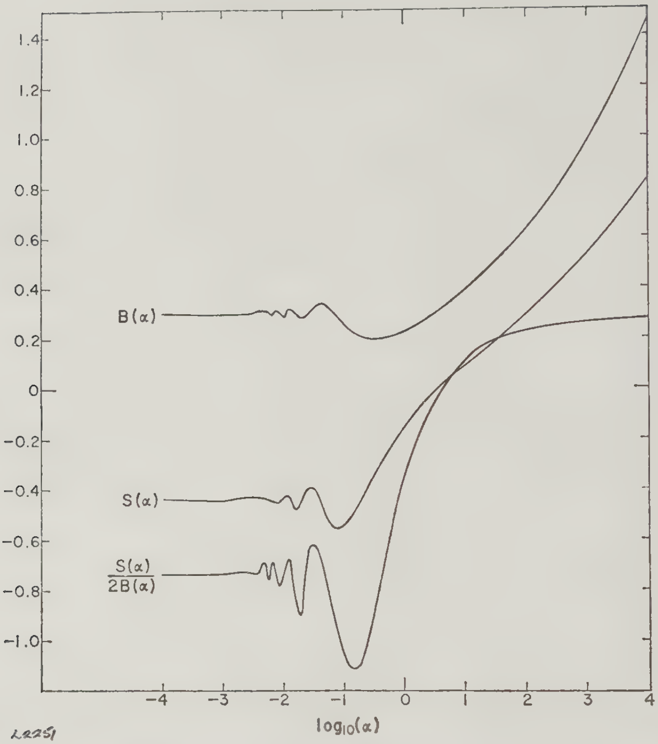

FIG. 2. The functions $S(\alpha)$, $B(\alpha)$ and $S(\alpha)/2B(\alpha)$ computed for a Lennard-Jones potential (Hindmarsh *et al.*, 1967).

(iv) $V(R) = C_{12}R^{-12} - C_8R^{-8} - C_6R^{-6}$. The effect of the dispersion term $-C_8R^{-8}$ has been investigated by Hindmarsh, du Plessis and Farr (1970). The phase shift function becomes

$$\eta(\rho) = \frac{63\pi}{256}\frac{C_{12}}{\hbar\bar{v}}\rho^{-11} - \frac{5\pi}{16}\frac{C_8}{\hbar\bar{v}}\rho^{-7} - \frac{3\pi}{8}\frac{C_6}{\hbar\bar{v}}\rho^{-5}$$
$$= \alpha x^{-11} - \xi x^{-7} - x^{-5}$$

where α and x are defined in eqns. (47) and (46), and

$$\xi = \frac{5\pi}{16}\left(\frac{8}{3\pi}\right)^{7/5} C_8(\hbar\bar{v})^{2/5}/C_6^{7/5} \qquad (52)$$

Hence

$$2\gamma = 8\pi \left(\frac{3\pi}{8}\right)^{2/5} N\bar{v}^{3/5} (C_6/\hbar)^{2/5} B(\alpha, \xi) \tag{53}$$

and

$$\beta = 2\pi \left(\frac{3\pi}{8}\right)^{2/5} N\bar{v}^{3/5} (C_6/\hbar)^{2/5} S(\alpha, \xi) \tag{54}$$

where

$$B(\alpha, \xi) = \int_0^\infty x \sin^2 \tfrac{1}{2} (\alpha x^{-11} - \xi x^{-7} - x^{-5}) \,\mathrm{d}x \tag{55}$$

and

$$S(\alpha, \xi) = \int_0^\infty x \sin (\alpha x^{-11} - \xi x^{-7} - x^{-5}) \,\mathrm{d}x. \tag{56}$$

Since it is clearly impossible to deduce all three constants from the two measured quantities γ and β, Hindmarsh *et al.* use a theoretical method for evaluating the parameter $C_8/C_6^{7/5}$ for each case investigated, using as a basis the work of Davison (1968), and requiring only the knowledge of the quantum numbers n^* and l for the two states involved in the transition. Then for a given ξ, the functions S and B can be computed and the constants C_6 and C_{12} deduced exactly as in (iii).

(v) Numerically calculated potentials. Attempts have recently been made to carry out numerical calculations of the interatomic potential with sufficient accuracy to use in line-broadening theories. The methods used for evaluating the interaction of atoms which combine chemically are not sufficiently accurate: it should be noticed that the depth of the potential well in many interesting cases of foreign gas broadening is only a few meV or less. Two methods of calculation which aim to give sufficient accuracy in the relevant region of interatomic distance have recently been proposed. The first (Roueff, 1970) treats the short-range part of interaction as essentially arising from the scattering of the valence electron of the radiating atom by the perturbing atom. The van der Waals interaction is added in separately. The expression for the short-range potential $V_s(R)$ involves the polarizability a_d of the perturber, the binding energy U of the valence electron of the radiator, a scattering length L and the probability $\phi^2(R)\mathrm{d}R$ that the valence electron is found in the spherical shell of radius R and thickness $\mathrm{d}R$, where R is the distance between radiating and perturbing atoms:

$$V_s(R) = 2\pi\ \phi^2(R) \left\{ \left[\frac{1}{L} - \frac{\pi a_d U}{3L^2} - \frac{4 a_d U^2}{3L} \ln \tfrac{1}{4}(a_d U)^{1/2} \right]^{-1} - \frac{\pi a_d U}{3} \right\}$$

where all quantities are expressed in atomic units.

The second set of numerical calculations is due to Baylis (1969). Here the noble gas atom is again treated as a polarizable dipole in order to find the long-range interaction, which behaves asymptotically as R^{-6}. The short-range interaction is calculated by means of a pseudopotential technique. The spin–orbit interaction is included, and so far only alkali–noble gas systems have been treated.

Once the potentials have been evaluated, it is a comparatively simple matter to use the Lindholm–Foley theory to calculate the broadening and shift. At the time of writing this has been done for the potentials calculated by Roueff; comparison with experiment will be dealt with in section 3B 1.

3. *The quasi-static approximation*

In this approximation, described in section 2A 3, the intensity of radiation at any frequency is proportional to the probability of occurrence of that frequency. Including the effect of multiple interactions (with the assumption of scalar additivity of the frequency perturbations) the result of these calculations is given by eqn. (18). We now apply this result to some specific interatomic potentials.

(i) $V(R) = \pm C_p R^{-p}$. Provided that $p > 3$, we have, using eqns. (15) and (17)

$$A(x) + iB(x) = \frac{4\pi N}{3} \exp\left[\frac{i\pi}{2}\left(2 - \frac{3}{p}\right)\right] (C_p/\hbar)^{3/p}\, \Gamma\left(1 - \frac{3}{p}\right) \mid x \mid^{3/p}$$

a result obtained by partial integration. Further progress requires the choice of a specific value for p.

(ii) $V(R) = -C_6 R^{-6}$. The integral $I(\Delta\omega)$ now takes the value 0 if $\Delta\omega$ is positive (since all perturbations are to low frequencies) and the value

$$I(\Delta\omega) = \frac{2\pi}{3} (C_6/\hbar)^{1/2} N \mid \Delta\omega \mid^{-3/2} \exp[-4\pi C_6 N^2/9\hbar \mid \Delta\omega \mid] \tag{57}$$

if $\Delta\omega$ is negative.

The intensity maximum occurs at

$$\Delta\omega_{\max} = -\frac{8\pi}{27} \frac{C_6}{\hbar} N^2,$$

showing that the quasi-static shift is proportional to the square of the perturber density for a van der Waals interaction. (This contrasts with the linear dependence of the impact shift.) On the high frequency side of the maximum the intensity drop is predominantly exponential; in the far low-frequency wing the variation is proportional to $|\Delta\omega|^{-3/2}$.

This latter result was obtained by Kuhn (1934) who drew attention to the fact that the far wing of a line, which is produced by close collisions, is largely formed as a result of binary encounters. If then the frequency perturbation $\Delta\omega = \omega - \omega_0$ is caused by a single perturber at R, the intensity in the range ω, $\omega + \mathrm{d}\omega$ may be equated to the probability of finding a lone perturber in the region R, $R + \mathrm{d}R$.

Thus $$I(\Delta\omega)\, \mathrm{d}\omega \propto R^2\, \mathrm{d}R \propto \mid \Delta\omega \mid^{-(3+p)/p} \mathrm{d}\omega$$

for a potential of the form $C_p R^{-p}$.

(iii) $V(R) = C_{12} R^{-12} - C_6 R^{-6}$. The more difficult problem of carrying out the quasi-static theory for a Lennard-Jones potential was first solved by Bergeon, Robin and Vodar (1952) and Bergeon (1954), who restricted their calculations to the region of high perturber density because of computational difficulties. Recently this work has been extended by Farr and Hindmarsh (1968) to the low density region.

As before, this work is done with the assumption that the individual frequency perturbations may be added scalarly. It is convenient to describe the potential in terms of its radius and depth parameters, σ and ϵ respectively, where

$$\sigma = (C_{12}/C_6)^{1/6}$$

$$\epsilon = (\tfrac{1}{4}C_6^2/C_{12}\hbar),$$

and then to work in terms of the reduced variables

$$t^2 = 4\epsilon x \tag{58}$$

$$\eta = \Delta\omega/4\epsilon \tag{59}$$

and

$$\delta = \pi N\sigma^3/3. \tag{60}$$

If we define a function

$$A'(x) + iB'(x) = [A(x) + iB(x)]\delta^{-1},$$

it is possible to write eqn. (18) in the form

$$I(\Delta)\omega = \int_0^\infty t\,\mathrm{e}^{-\delta A'(t)}\cos\{\delta B'(t) + \eta t^2\}\,\mathrm{d}t \tag{61}$$

apart from a constant factor.

The function $A'(t) + iB'(t)$ is given according to Bergeon *et al.* by the expression

$$\begin{aligned} A'(t) + iB'(t) = {} & \mathrm{e}^{i\pi/8}\,\Gamma(-\tfrac{1}{4})\,F(-\tfrac{1}{4}, \tfrac{1}{2}, -\tfrac{1}{4}it^2)\,t^{1/2} \\ & - \mathrm{e}^{-i3\pi/8}\,\Gamma(\tfrac{1}{4})\,F(\tfrac{1}{4}, \tfrac{3}{2}, -\tfrac{1}{4}it^2)\,t^{3/2} \end{aligned}$$

where $F(a, b, z)$ is the confluent hypergeometric function

$$F(a, b, z) = 1 + \frac{az}{b1!} + \frac{a(a+1)}{b(b+1)}\frac{z^2}{2!} + \ldots,$$

whereas Hindmarsh *et al.* use the equivalent form

$$A'(t) + iB'(t) = -t^{1/2}\sum_{k=0}^{\infty}\frac{1}{k!}\,t^k\,\Gamma(\tfrac{1}{2}k - \tfrac{1}{4})\,\mathrm{e}^{i(-\pi/8 - k\pi/4)}. \tag{62}$$

The integral $I\,(\Delta\omega)$ converges only slowly, especially at low values of perturber density (low δ), and can only be evaluated after a lengthy numerical computation, during which it is necessary to use an asymptotic approximation for A and B at large values of t. The profiles computed by Bergeon *et al.* are shown in Fig. 3, and those of Hindmarsh *et al.* in Fig. 4. The most noteworthy feature of this calculation is that at low δ, satellite bands appear on the low frequency wing at frequencies corresponding to $\omega_0 - \epsilon$, $\omega_0 - 2\epsilon$, ... They are, of course, here predicted to be much sharper than observed satellite features, as no impact broadening is included in the calculation (see section 2C 4). However, it is clear that the appearance of these bands, at least in some cases, is a purely statistical phenomenon, arising from the fact that the potential goes through a minimum at an energy corresponding to a frequency of $\omega_0 - \epsilon$.

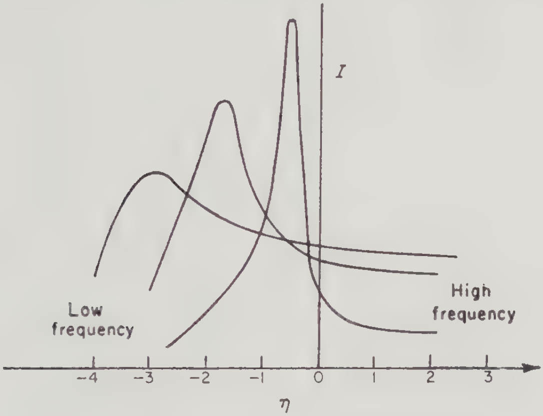

FIG. 3. The quasi-static theory intensity distribution for a Lennard-Jones potential. $\delta = 1.5, 0.8, 0.3$ in the three curves respectively. The highest density corresponds to about 100 atm and is the widest of the profiles (Bergeon *et al.*, 1952).

4. *Classical unified theory*

The difficulties inherent in a unified theory of pressure broadening, which describes the shift, width and shape of a spectral line under all

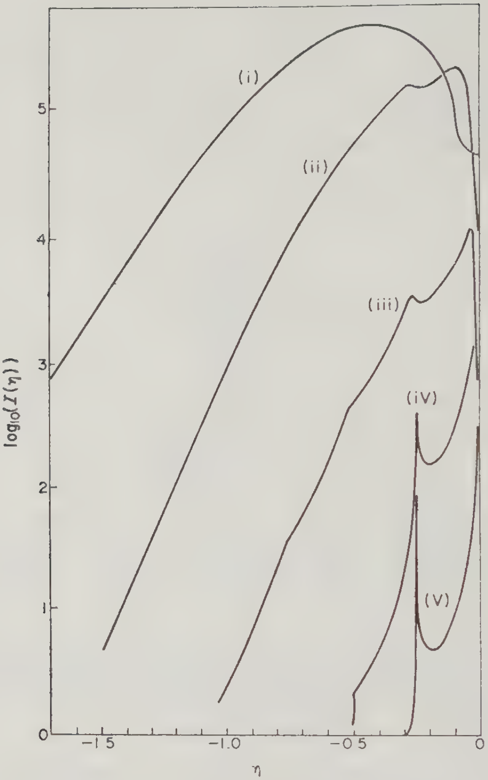

FIG. 4. The quasi-static theory intensity distribution for a Lennard-Jones potential. $\delta = 0.3, 0.1, 0.06, 0.01, 0.0014$ for (i), (ii), (iii), (iv), (v) respectively. The lowest value corresponds to a pressure of somewhat less than an atmosphere (Hindmarsh and Farr, 1969).

conditions and which is not subject to the restrictions of either the impact or quasi-static approximations, are such that no general analytic expression for the line shape can be found. The reader is referred to the review of Ch'en and Takeo (1957) for a description of the various approaches which had been tried before that date, all of which ultimately assumed $V(R) = -C_6R^{-6}$. Some recent attempts at approximating the unified theory for a Lennard-Jones potential are given below.

Behmenburg (1968) has repeated the work of Lindholm (1945), replacing the van der Waals potential by $V(R) = C_{12}R^{-12} - C_6R^{-6}$. Lindholm, whose work was the first unified theory to be proposed, writes

$$[\mathrm{e}^{i\eta(t,s)}]_t = \mathrm{e}^{-G(s)+iK(s)} \tag{63}$$

in which case the intensity distribution may be written, from eqns. (3) and (4)

$$I(\omega) = \int_0^\infty \mathrm{e}^{-G(s)} \cos \{K(s) + (\omega - \omega_0)s\}\, \mathrm{d}s. \tag{64}$$

The time-averaged exponential is then evaluated with the following assumptions:

1. The atomic radiation suffers frequency changes, and therefore phase changes, as a result of collisions between radiators and perturbers.
2. Perturbers, which are distributed randomly in space, follow straight paths with constant velocity relative to the optically active atoms.
3. The duration of a collision is proportional to the impact parameter.
4. Frequency perturbations caused by collisions which overlap in time are additive.
5. The phase change suffered during a collision, $\int_0^s \Delta\omega(t)\mathrm{d}t$, is taken to be a linear function of time. This is equivalent to approximating the complicated time dependence of $\Delta\omega(t)$ by a constant frequency change during the collision. (See Fig. 6.)

The method of evaluating $[\mathrm{e}^{i\eta(t,s)}]_t$ is described in some detail by Lindholm, who shows that

$$G(s) = \sum_{\tau_\rho=0}^{s} N\bar{v}\sigma_\rho \left[(1 - \cos \eta_\rho)(s - \tau_\rho) - \frac{2}{\kappa_\rho} \sin \eta_\rho + 2\tau_\rho\right]$$

$$+ \sum_{\tau_\rho=s}^{\infty} N\bar{v}\sigma_\rho \left[(1 - \cos \kappa_\rho s)(\tau_\rho - s) - \frac{2}{\kappa_\rho} \sin \kappa_\rho s + 2s\right] \tag{65}$$

and

$$K(s) = \sum_{\tau_\rho=0}^{s} N\bar{v}\sigma_\rho \left[(1 - \cos \eta_\rho)\frac{2}{\kappa_\rho} + (s - \tau_\rho) \sin \eta_\rho\right]$$

$$+ \sum_{\tau_\rho=s}^{\infty} N\bar{v}\sigma_\rho \left[(1 - \cos \kappa_\rho s)\frac{2}{\kappa_\rho} + (\tau_\rho - s) \sin \kappa_\rho s\right] \tag{66}$$

where for a collision of impact parameter ρ, τ_ρ is the collision time, κ_ρ the phase change per unit time during the collision, $\eta_\rho = \kappa_\rho\tau_\rho$ is the total phase change per collision and $\sigma_\rho = 2\pi\rho \mathrm{d}\rho$ is the cross-section for such a collision.

Now a collision with parameter ρ will produce (for an interaction of the Lennard-Jones type) the phase change given in section 2C 2 (iii) and, by assumption 3,

$$\tau_\rho = 2\chi\rho/\bar{v} \tag{67}$$

where χ is a constant of proportionality (≈ 1) which Behmenburg determines later by adjusting theory to experiment, so that

$$\kappa_\rho = \frac{\pi}{2\chi\hbar}\left(\frac{63}{256}\frac{C_{12}}{\rho^{12}} - \frac{3}{8}\frac{C_6}{\rho^6}\right) \tag{68}$$

Using the parameters

$$\zeta = \frac{\pi}{\bar{v}}\left(\frac{3C_6}{8\hbar}\right)^{11/6} \Bigg/ \left(\frac{63}{256}\frac{C_{12}}{\hbar}\right)^{5/6} \tag{69}$$

and

$$z = \rho\zeta^{1/5}\left(\frac{8\bar{v}}{3\pi C_6}\right)^{1/5}, \quad (70) \qquad y = \frac{\bar{v}s}{2\chi}\zeta^{1/5}\left(\frac{8\bar{v}}{3\pi C_6}\right)^{1/5} \quad (71)$$

Behmenburg substitutes these various quantities into the expressions given above for $G(s)$ and $K(s)$, to obtain for the intensity distribution in the line

$$I(\omega) = \int_0^\infty e^{-\{\zeta^{-3/5}\, 2h\phi(\zeta, y)\}} \cos\{\zeta^{-1/5}\, ky + \zeta^{-3/5}\, h\psi(\zeta, y)\}\, dy \quad (72)$$

where $h = 4\pi N\chi(3\pi C_6/8\bar{v})^{3/5}$

and $k = (\omega - \omega_0)\,(\chi/\bar{v})\,(3\pi C_6/8\bar{v})^{1/5}$.

The functions $\phi(\zeta, y)$ and $\psi(\zeta, y)$ are integrals given by

$$\phi(\zeta, y) = \int_0^y [(1 - f_1\,(\zeta, z))\,(y - z) - f_2\,(\zeta, z)\, h_0\,(\zeta, z) + 2z]\, z\mathrm{d}z$$

$$+ \int_y^\infty [(1 - g_1\,(\zeta, z, y))\,(z - y) - g_2\,(\zeta, z, y)\, h_0\,(\zeta, z) + 2y]\, z\mathrm{d}z$$

$$\psi(\zeta, y) = \int_0^y [(1 - f_1(\zeta, z)\, h_0(\zeta, z)) + f_2(\zeta, y)\,(y - z)]\, z\mathrm{d}z$$

$$+ \int_y^\infty [(1 - g_1(\zeta, z, y))\, h_0(\zeta, z) + g_2(\zeta, z)(z - y)]\, z\mathrm{d}z$$

where $f_1(\zeta, z) = \cos\,[2\zeta(z^{-5} - z^{-11})]$, $f_2(\zeta, z) = \sin\,[2\zeta(z^{-5} - z^{-11})]$

$g_1\,(\zeta, z, y) = \cos\,[2\zeta y(z^{-6} - z^{-12})]$, $g_2(\zeta, z, y)$

$= \sin\,[2\zeta y(z^{-5} - z^{-12})]$

and $h_0(\zeta, z) = z^{12}/\zeta(1 - z^6)$

Only for sufficiently small y are the functions $\phi(\zeta, y)$, $\psi(\zeta, y)$ in closed mathematical form, in which case they may be written

$$\phi(\zeta, y) = 0.450\, \zeta^{1/4}\, y^{1/4} + 0.437\zeta^{1/6}\, y^{7/6}$$

and

$$\psi(\zeta, y) = -(0.187\ \zeta^{1/4}\ y^{1/4} + 0.117\ \zeta^{1/6}\ y^{7/6}).$$

For sufficiently large y, the functions are linear in y; at intermediate values they have to be computed numerically.

The validity of this calculation may be tested by deduction of the special case of the impact and quasi-static limits and the far wing shape at low perturber density, and by comparison with experiment. The comparison with experiment is described in section 3 of this review, and in the impact limit (small h and k) it may easily be shown that the intensity distribution here agrees with that of impact theory. To the authors' knowledge the deduction from the general expression above of the quasi-static case and of the far wing shape has not been carried out.

A different approach to the problem of the unified theory has been used by Fox and Jacobson (1969). Starting from the usual expression

$$I(\omega) = \int_{-\infty}^{+\infty} \Phi(s) e^{i\omega s}\, ds$$

for the intensity distribution, these authors write the correlation function (assuming scalar additivity of the perturbations):

$$\Phi(s) = \left[\exp\left\{i \int_0^s \Delta\omega(t)\, dt - \tfrac{1}{2} M_R\, \overline{v^2}/kT\right\}\right]_{\text{Avge}}$$

where k is the Boltzmann constant, $\overline{v^2}$ is the mean square relative velocity of perturbers and radiators and M_R is the reduced mass. The averaging is then carried out over all initial positions and velocities of the perturbers, a procedure which makes the calculation essentially quasi-static in character.

Fox and Jacobson introduce the time-dependence of the interaction by expanding the potential $C_n R^{-n} - C_p R^{-p}$ in a power series in time (an idea suggested first by Holstein (1950)) and allowing the perturbers to follow classical paths with varying velocity during collision. Truncating the time expansion at terms in t^3, they obtain for the correlation function a complicated expression which has to be evaluated numerically. A further numerical integration gives the line profile. An important feature of this calculation is the inclusion of the Boltzmann factor: this is important for close collisions, that is large interaction energies, and therefore for the extreme wings of the lines which are most easily observed at high perturber gas densities.

This method of calculation produces the intensity distribution one would expect if all frequencies emitted had the same finite lifetime. This is clearly incorrect, as the configurations which give rise to these various frequencies have very different durations. At high perturber density this may well be of no consequence, since even a purely quasi-static calculation predicts a smooth profile which will be relatively unaffected by the introduction of non-infinite lifetimes for the configurations.

Takeo (1970) has made a calculation similar to that of Fox and Jacobson specifically for a Lennard-Jones potential, although the perturbers are assumed to follow straight paths. His calculated profiles, appropriate to perturber densities in excess of 10^{20} cm^{-3}, show a satellite band on the low frequency wing, which however is in poor agreement with experimental profiles.

A third different approach to the problem of finding a unified theory has been made by Hindmarsh and Farr (1969). Here the starting point is the quasi-static line profile, calculated for $V(R) = C_{12}R^{-12} - C_6R^{-6}$, which has already been discussed in section 2C 3. Using the fact that a Fourier analysis of a finite wavetrain of frequency ω, averaged over random lifetimes, yields a Lorentz profile with damping constant γ where γ^{-1} is the mean lifetime Hindmarsh and Farr give as an approximate expression for the line shape

$$I(\omega) = \int_0^\infty \frac{\gamma(\omega')/\pi}{(\omega - \omega')^2 + \gamma(\omega')^2} I_s(\omega')\, d\omega' \qquad (73)$$

where $\gamma(\omega')^{-1}$ is the mean duration of wavetrains of frequency ω', and $I_s(\omega')$ is the quasi-static intensity distribution. (The continuous change in ω' as a perturber flies past an optically active atom is not, of course, strictly equivalent to a sequence of values of ω' lasting for finite durations.)

For the purpose of calculating $I(\omega)$ the line is divided into two main regions, the impact region where the quasi-static calculation is invalid, and the quasi-static region where $I_s(\omega')$ forms a satisfactory starting point for the calculation of the profile. The boundary between these two regions on the low-frequency wing occurs at ω_g, where ω_g may be estimated as described in section 2A 2, eqn. (11). The contribution to $I(\omega)$ from $\omega > \omega_g$ (note that $\omega_g < \omega_0$) is calculated by taking $\int I_s(\omega')\mathrm{d}\omega'$ within the impact region and giving it a Lorentzian distribution of width 2γ and shift β calculated according to Hindmarsh *et al.* (1967) for the particular interaction potential under consideration. Since the quasi-static intensity on the high-frequency wing is very low, it may be set equal to zero, so that the line shape $I(\omega)$ is given by the expression:

$$I(\omega) = \int_0^{\omega_g} \frac{\gamma(\omega')/\pi}{(\omega - \omega')^2 + \gamma(\omega')^2} I_s(\omega')\,\mathrm{d}\omega' + \frac{\gamma}{\pi}\int_{\omega_g}^{\infty} \frac{I_s(\omega')\mathrm{d}\omega'}{(\omega - \omega_0 - \beta)^2 + \gamma^2}. \tag{74}$$

The mean lifetimes associated with the frequencies $\omega' < \omega_g$ are estimated on the basis of an idea advanced by Kuhn and London (1934), namely that the time-varying frequency $\omega(t)$ of a continuously perturbed wavetrain may be considered to remain $\omega(0)$ for so long as the phase of $\omega(t)$ does not differ from $\omega(0)$ by more than some arbitrary amount. Choosing this amount to be 1 radian, Hindmarsh and Farr define the semi-lifetime T of the frequency $\omega(0)$ by the condition

$$\int_0^T \omega(t)\,\mathrm{d}t - \omega(0)\,T = 1.$$

Then, replacing $\omega(t)$ by the first non-zero term (term n) in the Taylor expansion of $\omega(t)$ about the point $t = 0$, the condition for T becomes

$$T = \left\{\frac{n+1}{(\mathrm{d}^n\omega(t)/\mathrm{d}t^n)_{t=0}}\right\}^{1/(n+1)}.$$

Using this expression, the mean lifetimes for all frequencies between ω_g and $\omega_0 - \epsilon$, where ϵ is the depth of the Lennard-Jones potential, may be estimated by considering only the attractive part of the potential; the mean lifetime for the frequency $\omega_0 - \epsilon$ is calculated using the full expression for the potential, and this same value is used for all frequencies less than $\omega_0 - \epsilon$ (further out on the low-frequency wing). This last approximation is not serious as the low value of $I_s(\omega')$ in this region ensures that the major contribution to $I(\omega)$ comes from frequencies greater than $\omega_0 - \epsilon$.

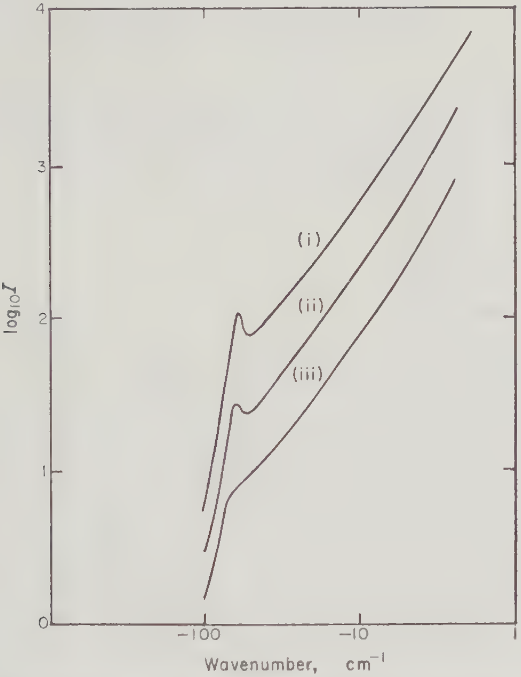

FIG. 5. The quasi-static theory intensity distribution corrected for the finite velocity of perturbers. $v = 2 \times 10^4$, 5×10^4 and 10^5 cm sec^{-1} for (i), (ii) and (iii) respectively. $\epsilon = 60$ cm^{-1}, $\sigma = 6$Å (Hindmarsh and Farr, 1969).

The final computation of $I(\omega)$ is achieved by numerical integration of the expression given above. The comparison of this calculated line profile with an experimental profile is described in section 3; here

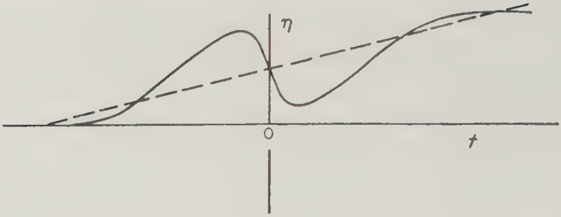

FIG. 6. The time dependence of the phase shift during a collision for a Lennard-Jones potential. The full line represents the true variation and the dotted line the linear approximation.

(in Fig. 5) is shown the predicted behaviour of the low-frequency wing for a particular potential for three different values of $\bar{v}$. Clearly, the satellite band becomes narrower and more prominent at lower temperatures.

3. EXPERIMENT

A. General Considerations

A great deal of experimental work in the field of neutral atom collision broadening has been undertaken in the 14 years since the appearance of the 1957 review of Ch'en and Takeo. The discussion in this section is not by any means intended to include an exhaustive list of these experiments. Rather, we have chosen a limited number which we consider to illustrate the way in which experiment has influenced the development of theory in this interval, the degree of accord between theory and experiment now attainable, the extent to which quantitative information on interaction potentials may be extracted from collision broadening measurements, and those phenomena which so far are unexplained.

B. Impact Region Measurements

1. *Foreign gas broadening*

It is, of course, in the impact region where the experimental study of collision-broadened spectral lines is most easily interpreted quantitatively. With the theories of section 2, it is possible to determine the constants C_6 and C_{12} for an atom pair, where $C_{6,12} = (C_{6,12})_{\text{excited}} - (C_{6,12})_{\text{ground}}$. The entire analysis rests on the assumption that the van der Waals, (12,6) or (12,8,6) potential chosen is a good model for the interaction between a perturber and an optically active atom in either state: having accepted this, a determination of the excited state constants is made possible by combining collision broadening data with that, for example, obtained from elastic scattering experiments which provide ground state values of the constants.

It is usual for elastic scattering experiments to be interpreted in terms of a (12,6) potential, and a critical survey of available experimental results has been made by Bernstein and Muckerman (1967), who have published a list of "best" parameters of the ground state potential for a number of atom pairs. Table 1 has been drawn up from these values, and shows in addition the calculated values of $(C_6)_{\text{ground}}$ found with Unsöld's formula, which is given in section 2C.

TABLE 1.

Atom pair	ϵ 10^{-21} J	σ 10^{-8} cm	$(C_6)_{\text{ground}}$ 10^{-66} J cm^6 exp.	theor.
Li-A	0.92	3.7	20	18
Li-Kr	1.5	3.6	26	28
Li-Xe	2.4	3.8	45	44
Na-A	1.0*	3.8*	18*	20
Na-Kr	1.4	4.5	80*	30
Na-Xe	2.1	4.4	120*	49
K-A	1.0	3.8	30	27
K-Kr	1.4	4.5	90*	42
K-Xe	1.8	5.2	74	68

* Less reliable values.

Until about six years ago, in the absence of a theory of pressure broadening which coped with a more complex interaction, impact region experiments were interpreted exclusively in terms of the van der Waals potential, although as early as 1945 Kleman and Lindholm, after an investigation of the behaviour of the sodium resonance lines under the influence of argon, had concluded that this interaction is inadequate at small distances.

This conclusion was confirmed by Hindmarsh (1959, 1960) and Behmenburg and Kohn (1964). The latter authors measured the broadening of the resonance lines of sodium ($3^2S_{\frac{1}{2}}$–$3^2P_{3/2}$) and strontium (5^1S_0–5^1P_1) by various gases under flame conditions at about 2500 K, and found, particularly with helium as perturbing gas, that the measured collision widths deviated significantly from theoretical values. Hindmarsh, also using helium as foreign gas, examined both the resonance and intercombination lines of calcium (4^1S_0–4^1P_1, 4^1S_0–4^3P_1), which were both confined well within impact theory limits, and found that the ratio $2\gamma/\beta$, predicted to have the value -2.75 for a van der Waals interaction, was 35 ± 15 for the resonance line and 7.5 ± 2 for the intercombination line. Concluding that short range repulsive forces must necessarily be taken into account for a meaningful interpretation of collision broadening, Behmenburg (1964) and Hindmarsh *et al.* (1967) published theoretical papers based on the (12,6) potential. These have been described in section 2C.

Since 1964, several experimental studies of impact region collision broadening have been interpreted in terms of a (12,6) interaction. The first of these was Behmenburg's (1964) study of the sodium line ($3^2S_{1/2}$–$3^2P_{3/2}$) perturbed by helium and by argon. In the case of argon, the shift-to-broadening ratio lies on the oscillating part of the $S(\alpha)/2B(\alpha)$ curve, and so the interaction constants cannot be determined unambiguously. In the case of helium, the measured C_6 of $(33 \pm 10) \times 10^{-66}$ J cm^6 is anomalously large compared to the theoretical value of 2.9×10^{-66} J cm^6, and the shift to a lower frequency is unusual for this perturber. However, the collision broadening of alkali-metal doublets is not well understood because of the possibility of collision-induced transitions, a problem which is discussed below.

Singlet lines of alkaline-earth elements, being free of such effects, are more convincingly interpreted, and Smith (1967) investigated the calcium intercombination line (4^1S_0–4^3P_1) formed in absorption in atmospheres of helium, neon, argon and krypton at temperatures of approximately 1030K and perturber densities up to 7×10^{18} cm^{-3}. In all cases, impact region conditions were well satisfied with shift and broadening varying linearly with perturber density. The results were interpreted using the Hindmarsh *et al.* (1967) version of the Lindholm–Foley theory for a (12,6) potential. The following interaction constants were obtained:

Atom pair	C_6 10^{-66} J cm^6	C_{12} 10^{-109} J cm^{12}
Ca-He	2.0 ± 0.2	0.97
Ca-Ne	1.8 ± 0.2	1.1
Ca-A	10.8 ± 0.8	7.4
Ca-Kr	25 ± 2	54

These C_6 values are all higher than the theoretical values by a factor of about 2, a result which is attributed by Hindmarsh *et al.* (1970) to the neglect of higher order dispersion terms in the interatomic interaction (see below).

A searching test of the validity of the (12,6) potential in the interpretation of collision broadening was applied by Vaughan and Smith (1968), who studied the red line of krypton ($4p^5(^2P_{3/2})\ 5s[\frac{3}{2}]_2 - 4p^5$ $(^2P_{3/2})\ 5p[\frac{3}{2}]_2$) perturbed by low pressures of helium, neon, argon and krypton at temperatures of 80K and 295K. They were thus able to test the complex temperature dependence predicted by Hindmarsh *et al.* as well as to measure the interaction constants. The shift-to-broadening ratios at the two temperatures were fitted as closely as possible to the theoretical $S(\alpha)/2B(\alpha)$ curve, with the restriction that each pair should show the correct temperature dependence. The corresponding values of $S(\alpha)$ and $B(\alpha)$ were then used to predict the temperature effects in shift and broadening individually. These are compared in the following list:

	Shift at 295K/Shift at 80K		Width at 295K/Width at 80K	
Perturber	Observed	Predicted	Observed	Predicted
He	2.62	2.16	1.87	1.73
Ne	0.93	0.84	1.67	1.70
A	2.29	1.79	2.07	1.64
Kr	1.47	1.43	1.48	1.43

Only in the case of argon does a serious discrepancy arise, which Vaughan and Smith suggest may be due either to the inadequacy of the theoretical treatment for potentials which are neither deeply attractive nor sharply repulsive, or to the wrong choice of interaction potential. To test the latter possibility, they calculated the $S(\alpha)$, $B(\alpha)$ curves for (10,6) and (18,6) potentials, but neither made much difference in the argon region. The observed C_6 values are in satisfactory agreement with the Unsöld calculations:

Atom pair	C_6 (10^{-66} J cm^6)	
	Observed	Predicted
Kr-He	4.5	4.7
Kr-Ne	15.9	8.6
Kr-A	24.5	35.4
Kr-Kr	54.6	53.8

The study of alkali–metal doublets has been pursued since the early days of experimental collision broadening (Füchtbauer and Gössler, 1933; Watson and Margenau, 1933; Hull, 1936; Peterman, 1933; Ny and Ch'en, 1937), and a striking feature of all such measurements is the existence of apparently unpredictable differences between components of the same doublet perturbed by the same gas. Schuller and Oksengorn (1969a) have calculated the *j*-dependence of the broadening and shift in the impact approximation (using only dispersion terms in the interaction) and have shown that the $^2P_{1/2}$ component behaves as in Lindholm's theory, but for the $^2P_{3/2}$ component there is a variation due to the anisotropy of the excited state interaction. Applying their calculation to the case of the broadening of the sodium resonance lines by argon, they find that the calculated shifts are in good agreement with those measured by Kleman and Lindholm, but that there is a discrepancy in the half-widths. The interference with the collision broadening process by collisional excitation transfer between the fine structure levels is regarded by some authors as being fundamental to this problem, and both theoretical (Callaway and Bauer, 1965) and experimental (Krause, 1966; Jordan and Franken, 1966) evidence shows that the

TABLE 2.

	Helium		Neon		Argon		Krypton		Xenon		Nitrogen		Carbon tetrafluoride	
	Width	Shift	Width	Shift	Width	Shift	Width	Shift	Width	Shift	Width	Shift	Width	Shift
Na 5896 $P_{1/2}$					0.742	−0.196					0.49	−0.214		
5890 $P_{3/2}$					0.689	−0.213					0.49	−0.223		
K 7699 $P_{1/2}$					1.01	−0.42					0.82	−0.36		
7665 $P_{3/2}$					1.01	−0.36					0.82	−0.30		
K 4047 $P_{1/2}$	1.45		0.71		2.20	−9.2					1.65	−0.83		
4044 $P_{3/2}$	2.02		0.82	−0.16	2.58	−8.3					1.89	−1.02		
Rb 7947 $P_{1/2}$	0.595	+0.228			0.627									
7800 $P_{3/2}$	0.735	−0.092			0.855									
Rb 4216 $P_{1/2}$	2.77	+0.93	1.30	+0.22	2.21	−1.2					1.51			
4202 $P_{3/2}$	1.88	+0.43	0.73	−0.16	2.56	−1.0					1.01			
Cs 8943 $P_{1/2}$		+0.128		−0.04	0.30	−0.238	0.28	−0.20	0.49	−0.25				−0.29
8521 $P_{3/2}$		+0.015		−0.08	0.30	−0.215	0.28	−0.20	0.23	−0.25				−0.23
Cs 4593 $P_{1/2}$		+0.51				−0.70	1.1	−0.62		−0.65				
4555 $P_{3/2}$		+0.26				−0.63	3.2	−0.62		−0.65				

All units are cm^{-1} (rel. density)$^{-1}$. Additional measurements are reported by Ch'en *et al.* for broadening by krypton in the 3rd and 4th Cs doublets, and shifts of $^2P_{3/2}$ up to the 20th doublet. Relative density is defined as the ratio of the actual density of the gas to the density the same gas would have at 0°C and 760 torr.

cross-sections for these two processes are of comparable size. However, Schuller and Oksengorn (1969b) show that this process has a marginal effect, measurable only in lithium.

A recent comprehensive study of the pressure broadening of the first few lines of the principal series of caesium by helium, neon, argon, krypton, xenon and carbon tetrafluoride has been undertaken by Ch'en, Garrett, Gilbert and co-workers (1966 I, II; 1967 III, IV; 1969 V, VI). Measurements have been made over a wide density range, from the impact region up to pressures of 300 atm in some cases. The general features of these results are explained by recent classical unified theories (see below). The low density measurements, the results of which are summarized in Table 2, along with the results of some of the earlier work mentioned above, are not interpreted quantitatively because of some unusual features, which include non-linearity of the broadening vs. density curves near the origin and an apparently very strong temperature effect on the broadening at higher densities. There is a possibility that both of these effects are experimental: the non-linearity arising from the uncorrected effect of hyperfine splitting and instrumental slit width, which amount to some 0.6 cm^{-1}, and the temperature effect arising from analysis of lines whose peak absorption is in excess of 50%. There is some evidence that heavily absorbed profiles can cause overestimated line widths (McCartan, 1970).

Rostas and Lemaire (1971) have measured the caesium doublet 6^2S-7^2P broadened by helium and argon. These measurements, made at low pressure, represent an improvement on those of Ch'en and Garrett, and are quoted in Table 5.

McCartan and Hindmarsh (to be published) have made a detailed investigation of the second doublet of the potassium principal series ($4^2S_{1/2} - 5^2P_{1/2,\ 3/2}$) formed in absorption in atmospheres of helium, argon and krypton under strict impact region conditions. The results

TABLE 3.

	Helium		Argon		Krypton	
	Width	Shift	Width	Shift	Width	Shift
4044 $P_{3/2}$	7.08 ± 0.2	0.37 ± 0.02	8.0 ± 0.1	−2.22 ± 0.03	5.50 ± 0.15	−1.97 ± 0.05
4047 $P_{1/2}$	4.94 ± 0.04	1.22 ± 0.02	7.54 ± 0.05	−1.75 ± 0.08	6.6 ± 0.2	−1.84 ± 0.05

Units of 10^{-20} cm^{-1} (cm^{-3})$^{-1}$.

of this study are summarized in Table 3. It was found that not all of these could be fitted to the $S(\alpha)/2B(\alpha)$ curves, a fact which the authors attribute to the inadequacy of the "straight path" approximation in these cases. The interaction constants deduced by McCartan *et al.* are

	C_6 J cm^6		C_{12} J cm^{12}	
	$P_{1/2}$	$P_{3/2}$	$P_{1/2}$	$P_{3/2}$
He	—	9.2×10^{-65}	—	7.6×10^{-106}
A	—	6.6×10^{-64}	—	5.8×10^{-106}
Kr	4.8×10^{-64}	4.5×10^{-64}	1.2×10^{-106}	2.3×10^{-106}

Combining these figures with the ground state measurements quoted earlier, the excited state constants are

	$(C_6)_{ex}$ J cm^6		$(C_{12})_{ex}$ J cm^{12}	
	$P_{1/2}$	$P_{3/2}$	$P_{1/2}$	$P_{3/2}$
He	—	9.5×10^{-65}	—	7.6×10^{-106}
A	—	6.9×10^{-64}	—	5.8×10^{-106}
Kr	6.2×10^{-64}	5.5×10^{-64}	1.4×10^{-99}	2.3×10^{-106}

The experimental facts regarding collision broadening in alkali doublets may be summarized as follows:

1. The difference in shift of the fine structure components depends on series member and perturber, not on the nature of the alkali.
2. Where there is a high-frequency shift, the $^2P_{1/2}$ component is shifted more than the $^2P_{3/2}$. The ratio is larger for the first series member than the second.
3. Differences in shifts to low frequencies are usually small, and there is apparently no way of knowing which component shows the stronger shift.

4. The broadening of the $^2P_{3/2}$ component is normally slightly greater than that of the $^2P_{1/2}$ component, although exceptions are found.

An important consideration in assessing the usefulness of collision broadening measurements is the degree of accord between the measured constants and the theoretically expected values. The constant C_{12} is not a reliable guide, as the "theoretical" value is in fact a semi-empirical value (see section 2C). The constant C_6 is a different matter, as theoretical estimates are more reliable, and any discrepancy must throw doubt on the validity of collision broadening theory. Table 4 shows, in columns four and five, the sort of agreement which is found between theoretical C_6 values and those deduced from collision broadening experiments using the Lindholm–Foley treatment for a (12,6) potential. On the whole, the experimental C_6 values exceed the theoretical ones by factors of about two or three. The last column shows the experimental values when a (12,8,6) potential is assumed. There is in general an improvement, which lends support to the idea that higher terms in

TABLE 4.

Author	Line	Perturber	C_6 theoretical 10^{-65} J cm^6	C_6 experimental 10^{-65} J cm^6 (12,6)	C_6 experimental 10^{-65} J cm^6 (12,8,6)
(1)	Ca 6573	He	0.062	0.2 ± 0.02	0.10 ± 0.02
(1)	Ca 6573	Ne	0.113	0.18 ± 0.02	0.10 ± 0.02
(1)	Ca 6573	A	0.46	1.08 ± 0.08	0.23 ± 0.02
(1)	Ca 6573	Kr	0.70	2.53 ± 0.2	0.61 ± 0.06
(2)	Ca 4227	He	0.30	0.3 ± 0.1	0.18 ± 0.06
(3)	A 6965	A	2.4	9 ± 4	2.9 ± 3
(4)	K 4047	Kr	38.1	52 ± 15	30 ± 9
(5)	Sr 4607	A	2.62	4.3 ± 0.4	2.8 ± 0.8
(6)	Kr 7601	He	0.47	0.45 ± 0.09	0.36 ± 0.07
(6)	Kr 7601	Ne	0.86	1.59 ± 0.3	0.81 ± 0.15
(6)	Kr 7601	A	3.54	2.45 ± 0.5	1.05 ± 0.2
(6)	Kr 7601	Kr	5.38	5.46 ± 1.1	4.4 ± 1

(1) Smith (1967); (2) Hindmarsh (1959); (3) Hindmarsh and Thomas (1961); (4) McCartan and Hindmarsh (1969); (5) Farr and Hindmarsh (1971); (6) Vaughan and Smith (1968).

the dispersion interaction (R^{-8}, R^{-10} . . .) may not be negligible in the excited state. Finally, the calculations of Roueff (1970) have been compared with experiment by Rostas and Lemaire (1971) for the caesium line λ4593 ($6^2S_{1/2} - 7^2P_{1/2}$) broadened by helium and argon. The calculations, which do not include spin–orbit interaction, are not expected to apply to the other component of the doublet, λ4555, which was, however, also measured. Table 5 compares the results of Rostas and Lemaire with the calculation of Roueff, and shows the agreement to be highly satisfactory.

2. *Resonance broadening*

Resonance broadening calculations in the impact approximation predict that pure resonance broadened lines are Lorentzian in shape with half-intensity width in radian s^{-1} of

$$2\gamma = k_{jj'} \left(\frac{2j+1}{2j'+1}\right)^{1/2} \frac{4\pi e^2 f_{jj'} N}{m\omega_0}$$

where N is the atom density, $f_{jj'}$ and ω_0 the oscillator strength and angular frequency respectively of the resonance line and j,j' are the angular momentum quantum numbers of the ground state and resonance state respectively. The width is independent of temperature, and the shift is predicted to be zero. (See the review of resonance broadening by Kuhn and Lewis (1969).) The value of the constant $k_{jj'}$ depends on j,j' and the approximations made in the calculation. Some recent values are:

	$k_{0,1}$	$k_{1/2,\,3/2}$	$k_{1/2,\,1/2}$	$\dfrac{k_{1/2,\,3/2}}{k_{1/2,\,1/2}}$
Ali and Griem (1965, 1966)	1	1	1	1.00
Omont and Meunier (1968)	1.04	—	—	—
Stacey and Cooper (1969)	1.04	1.04	0.903	1.15

Because of the difficulties of self-absorption in emission lines, most measurements made directly on resonance lines (largely in the case of

TABLE 5.

Cs line	Gas		Experiment Rostas and Lemaire (1971)	Theory Roueff (1970)
λ4593		$2\gamma/N$	8.8 ± 0.5	9.2
$6^2S_{1/2}$–$7^2P_{1/2}$	He	β/N	$+1.5 \pm 0.1$	
		$2\gamma/\beta$	$+5.85$	$+6.3$
λ4555		$2\gamma/N$	6.9 ± 0.4	
$6^2S_{1/2}$–$7^2P_{3/2}$	He	β/N	$+0.73 \pm 0.05$	
		$2\gamma/\beta$	$+9.45$	
λ4593		$2\gamma/N$	6.7 ± 0.5	4.9
$6^2S_{1/2}$–$7^2P_{1/2}$	A	β/N	-1.63 ± 0.05	
		$2\gamma/\beta$	-4.1	-11.6
λ4555		$2\gamma/N$	5.8 ± 0.3	
$6^2S_{1/2}$–$7^2P_{3/2}$	A	β/N	-1.55 ± 0.06	
		$2\gamma/\beta$	-3.74	

γ/N and β/N are in units of 10^{-20} cm^{-1}/cm^{-3}.

alkali metals) have been made in absorption. Moser and Schulz (1959) have tabulated the experimental results available at that time, and discrepancies amounting to several orders of magnitude occur between different experiments and between experiment and theory. Since then, Ya'akobi (1966, 1968) has made measurements on the resonance lines of lithium, but these results also seem to be not very quantitative.

A more accurate technique involves the indirect study of the broadening of a resonance level by making measurements on an emission line whose lower state is the resonance level. Quantitative results were first obtained this way by Hindmarsh and Thomas (1961), who investigated the self-broadening in argon and were able to estimate the oscillator strength of the resonance line λ1048 by studying the self-broadening of the line λ8264. Lewis, Rebbeck and Vaughan (1969) adopted the same method and measured the resonance broadening of the 4^2P states of potassium by studying in emission the lines ($4^2P_{1/2,3/2} - n^2S_{1/2}, n = 6, 7, 8$). This gave the values $k_{1/2,3/2} = 1.33 \pm 0.3$, $k_{1/2,1/2} = 1.24 \pm 0.3$, with the ratio $k_{1/2,3/2}/k_{1/2,1/2} = 1.09 \pm 0.06$.

Kuhn and his co-workers (Kuhn and Vaughan, 1964; Kuhn and Lewis, 1967; Vaughan, 1966a, b, 1968; Stacey and Vaughan, 1964) have made a major investigation of resonance broadening in the inert gases helium, neon, argon and krypton using this indirect technique, with the object of testing the results of theory. In all cases studied the variation of half-width with density was very close to linear over a density range of $10^{16} - 4 \times 10^{17}$ cm^{-3}. The results obtained for lines leading to the upper state of a strong resonance line are given in Table 6.

TABLE 6.

Element	λ Å	Transition	$2\gamma/N$ at 80K 10^{-20} cm^{-1}(cm^{-3})$^{-1}$	$2\gamma/N$ at 280K 10^{-20} cm^{-1}(cm^{-3})$^{-1}$	β/N 10^{-20} cm^{-1}(cm^{-3})$^{-1}$
He	7281	$2^1P_1–3^1S_0$	7.85 ± 0.4	8.1 ± 0.6	0 ± 0.1
	6678	$2^1P_1–3^1D_1$	7.8 ± 0.4	7.9 ± 0.5	0 ± 0.05
Ne	6678	$^1P_1–^2P_4$	6.27 ± 0.15	6.2 ± 0.3	0 ± 0.1
A	7503	$^1P_1–^2P_1$	15.66 ± 0.7	15.0 ± 0.7	0 ± 0.2
	7514	$^3P_1–^2P_5$	3.6 ± 0.3	3.9 ± 0.4	0.07 ± 0.03
Kr	7685	$^1P_1–^5p_1$	10.8 ± 0.5	11.0 ± 0.6	0 ± 0.5
	7587	$^3P_1–^5p$	12.8 ± 0.2	13.1 ± 0.6	0.1 ± 0.1

In all cases there is large broadening, no measurable shift and no measurable temperature effect. Other lines were measured which are transitions to a weak resonance level, and these show 5–10 times smaller broadening, an increase of broadening with temperature and a non-zero shift: in these lines a higher order interaction interferes with the resonance broadening.

The case of helium is particularly interesting as the oscillator strength of the resonance line has been computed very accurately by Schiff and Pekeris (1964), so that the measured resonance broadening leads to a value of $k_{0,1}$. This value, 0.99 ± 0.06, is in excellent agreement with recent theoretical values; Omont and Meunier (1968) considers the value 1.45 to be accurate to ± 0.04. Using this value of $k_{0,1}$ oscillator strengths of the resonance lines of neon, argon and krypton have been derived from resonance broadening measurements, and are in satisfactory agreement with theory.

An interesting phenomenon has shown up in these rare gas experiments, namely that the Lorentz width extrapolated to zero density is significantly higher than the expected natural width. This "extrapolation anomaly" has been explained by Kuhn, Lewis and Vaughan (1965) in terms of an additional coupling width.

The technique of resonance fluorescence may be used to make accurate measurements of self-broadening in certain favourable cases. Such experiments involving $^3P_1$ resonance levels have been performed by Omont and Meunier (1968) and by Happer and Saloman (1967). The $k_{jj'}$ values are different for the orientation and alignment signals; the theoretical value for the alignment broadening is $k = 1.32$. Omont's study of the 6^3P_1 level in mercury, and Happer and Saloman's investigation of the $^3P_1$ resonance in lead both give good agreement with this value of k within experimental accuracy, and the latter authors further find the ratio of the broadening constants for the orientation and alignment signals to be 1.21 ± 0.05, compared with a theoretical ratio of 1.25.

Little work on resonance broadening has been done at higher densities where the impact theory is invalid. The quantum mechanical calculations of Mead (1960) and Reck, Takabe and Mead (1965) predict a lowering of the resonance level and a linear variation of γ with $\sqrt{N}$. These facts are not inconsistent with the experiments of Vaughan (1968) and Lauriston and Welsh (1951).

C. Non-impact Region Measurements.

Since Minkowski (1935) first showed that the intensity distribution in the far low-frequency wing of the sodium resonance lines perturbed by argon was of the $\Delta\omega^{-3/2}$ form, numerous experiments have provided data concerning the non-impact region of pressure broadening: we discuss here only a few of the more recent of these.

Granier and his co-workers have presented, in a series of papers (1961, 1963a, b, 1965a, 1966a, b), the results of a study of the influence of perturber mass and temperature on the broadening and shift of the resonance lines of mercury and the alkali metals at high perturber density, and have come to the conclusion that, especially when dealing with light atoms, repulsive forces cannot be neglected. This result, of course, parallels the work of Behmenburg and Hindmarsh in the impact region. Proper comparison of theory and experiment outside the impact region, however, has only been possible since the development of a (12,6) unified theory, and the experiments which have been quantitatively assessed in this way are so far only those of Ch'en *et al.* on the behaviour of the caesium resonance lines when perturbed by argon and neon (see section 3B), and the study of McCartan *et al.* of the low frequency wing of the potassium line (4^2S_0–$5^2P_{1/2}$) perturbed by krypton.

Ch'en's work has been interpreted by Behmenburg (1968), who has considered the effects of both neon and argon, and by Fox and Jacobson (1969), whose calculations apply to broadening by argon only. Figures 7, 8 and 9 show respectively the half-intensity width, shift and asymmetry of the caesium line (6^2S_0–$6^2P_{1/2}$) as a function of relative density

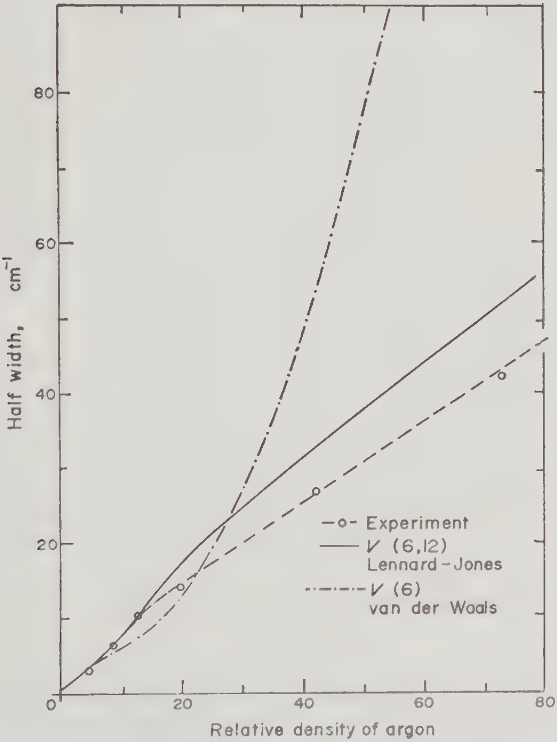

FIG. 7. A comparison of theory and experiment in the pressure broadening of Cs λ8943 by argon (Behmenburg, 1968).

of argon (density relative to that at N.T.P.) obtained experimentally by Ch'en and calculated by Behmenburg. The C_6 and C_{12} values used in the calculation are obtained by Behmenburg from the low-density measurements (corrected for the effects of hyperfine structure and slit width) using the well-established (12,6) impact theory. The value of the factor χ (see section 2C), which fixes the assumed collision time, is chosen by Behmenburg by forcing a fit between the experimental and theoretical parameters at some characteristic point. In the case of argon,

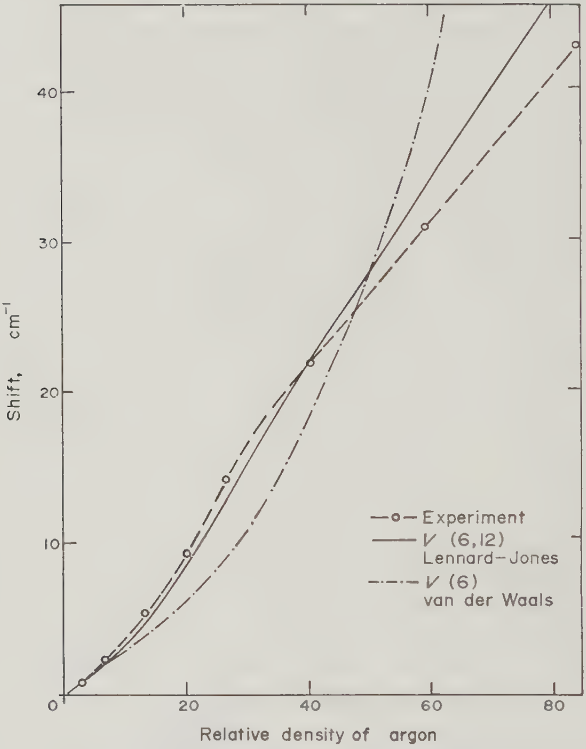

FIG. 8. A comparison of theory and experiment in the pressure shift of Cs λ8943 by argon (Behmenburg, 1968).

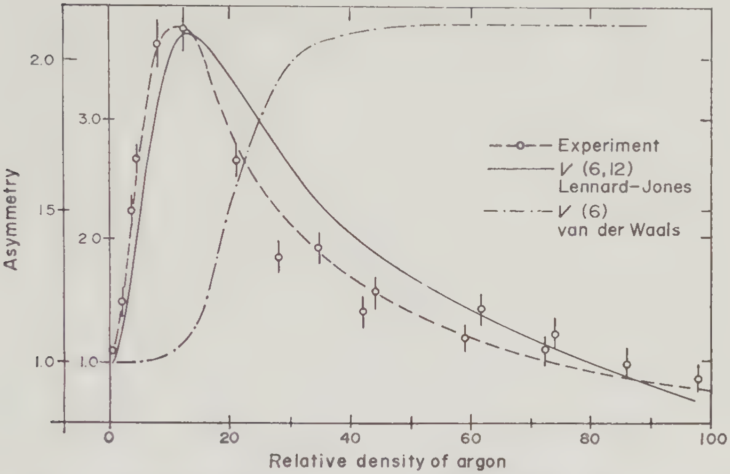

FIG. 9. The asymmetry of Cs λ8943 as a function of the argon pressure. The inner scale refers to the van der Waals potential (Behmenburg, 1968).

this point is that at which the asymmetry is a maximum. The calculations are thus based on the values

$$C_6 = 5.6 \times 10^{-65}\ \mathrm{J\ cm^6}$$

$$C_{12} = 3.0 \times 10^{-108}\ \mathrm{J\ cm^6}$$

$$\chi = 1.01.$$

Fox and Jacobson obtain, for the same line, the theoretical curves shown in Figs. 10 and 11 (along with the experimental points) by using

$$C_6 = 2.25 \times 10^{-65}\ \mathrm{J\ cm^6}$$

$$C_{12} = 4.59 \times 10^{-109}\ \mathrm{J\ cm^{12}}$$

The theoretical value of C_6 is 3.6×10^{-65} J cm^6.

Behmenburg has also interpreted the neon broadening, fixing χ by forcing a fit between experiment and theory where the relationship between shift and density goes through zero for the second time. The results, shown in Figs. 12, 13 and 14, are less good than for argon,

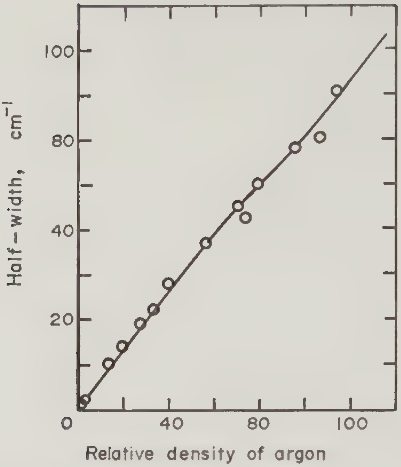

FIG. 10. A comparison of theory and experiment in the pressure broadening of Cs λ8943 by argon (Fox and Jacobson, 1969).

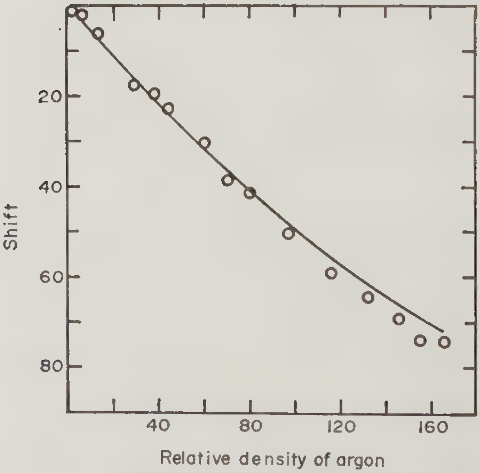

FIG. 11. A comparison of theory and experiment in the pressure shift of Cs λ8943 by argon (Fox and Jacobson, 1969).

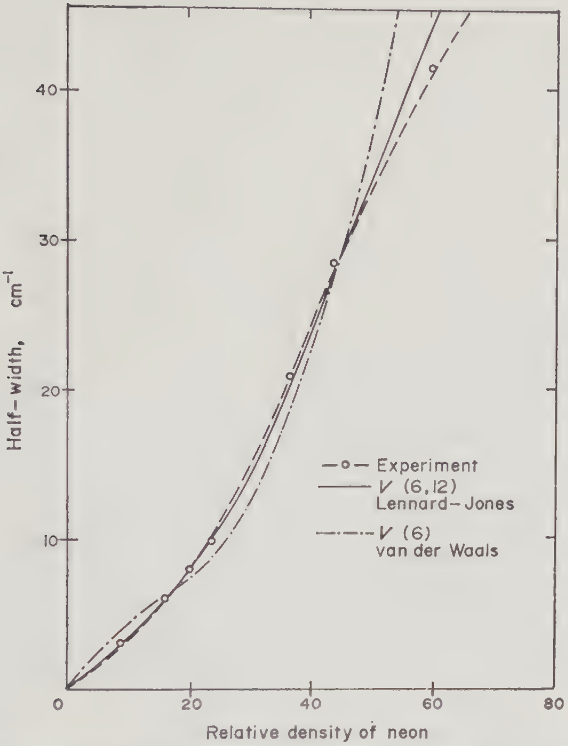

FIG. 12. A comparison of theory and experiment in the pressure broadening of Cs λ8943 by neon (Behmenburg, 1968).

which Behmenburg feels may be due to the inadequacy of the (12,6) potential in describing the neon–caesium interaction. The constants used are

$$C_6 = 1.59 \times 10^{-65}\ \mathrm{J\ cm^6}$$

$$C_{12} = 9.42 \times 10^{-108}\ \mathrm{J\ cm^{12}}$$

$$\chi = 1.18$$

and the theoretical value of C_6 is 0.91×10^{-65} J cm^6.

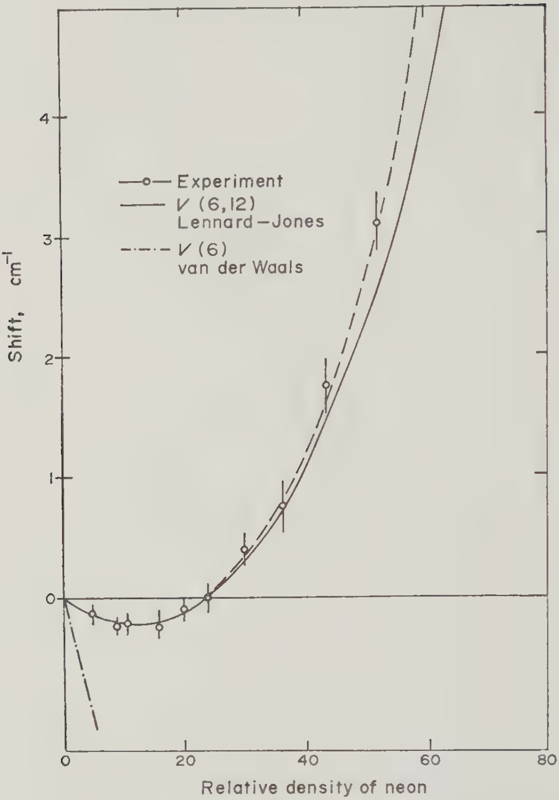

FIG. 13. A comparison of theory and experiment in the pressure shift of Cs λ8943 by neon. The inadequacy of the van der Waals potential is particularly evident in this case (Behmenburg, 1968).

McCartan *et al.* have, in contrast to Ch'en, studied a low-frequency wing profile at low perturber density, but at such large displacements from the unperturbed line that the impact theory is no longer applicable. Using the quasi-unified theory of Hindmarsh *et al.*, they have interpreted the shape of the $(4^2S_{1/2}\text{-}5^2P_{1/2})$ absorption line of potassium

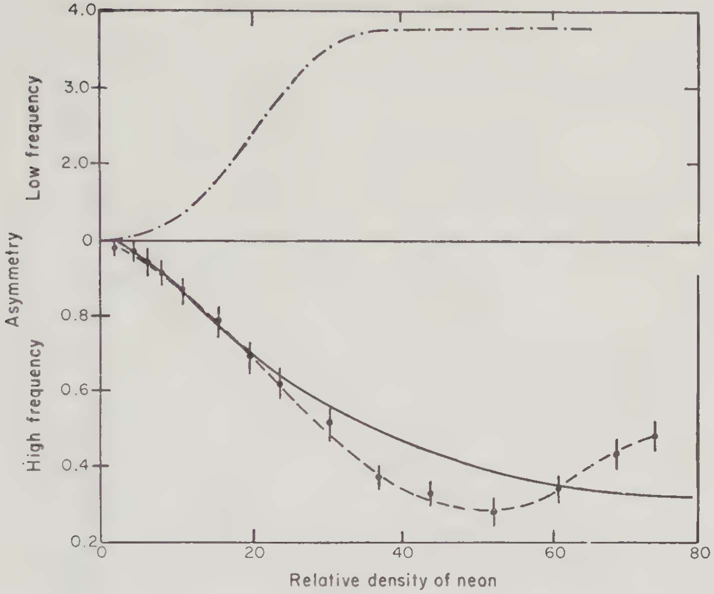

FIG. 14. The asymmetry of Cs λ8943 as a function of the neon pressure. The upper scale corresponds to the van der Waals potential (Behmenburg, 1968).

broadened by krypton as arising from a (12,6) interaction potential where

$$\epsilon = 27 \pm 1 \text{ cm}^{-1}$$

$$\sigma = (8.0 \pm 0.3) \times 10^{-8} \text{ cm},$$

which is in excellent agreement with the impact region result that

$$\epsilon = 25 \pm 2 \text{ cm}^{-1}$$

$$\sigma = (8.0 \pm 0.3) \times 10^{-8} \text{ cm}.$$

Figure 15 shows that the calculated and experimental profiles are in very good agreement over an intensity range of at least four orders of magnitude, including the prominent satellite band at about 25 cm^{-1} from the core. The contribution to the profile beyond the band is

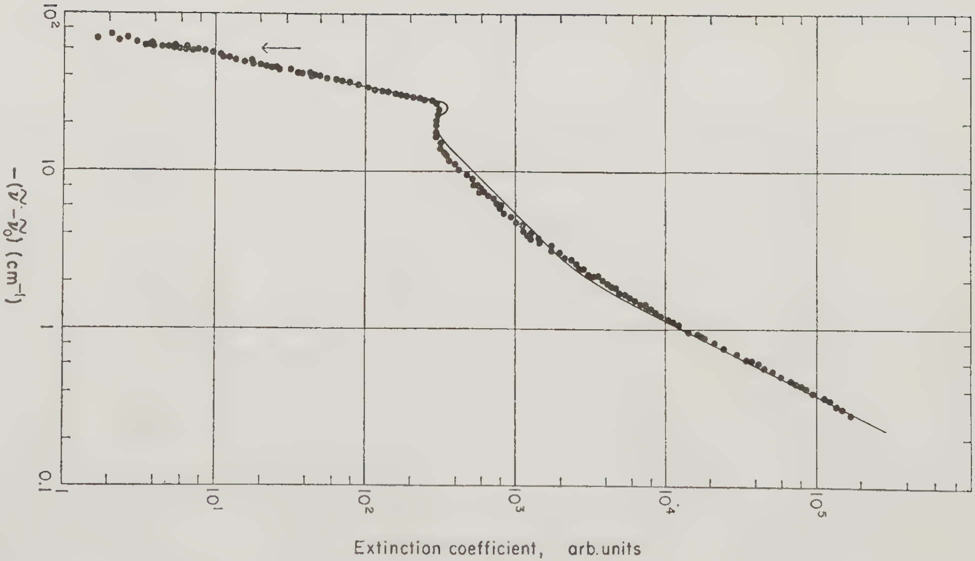

FIG. 15. A comparison of theory and experiment in the line shape of K λ4047 broadening by krypton (McCartan and Hindmarsh, 1969). The circles are the measured points and the line is the profile calculated by the method of Hindmarsh and Farr (1969).

almost entirely due to "impact" broadening of the band itself, due to the finite duration of the wavetrains absorbed at that frequency. There is some indication of a feature at about 50 cm^{-1}, which would be expected on the basis of the quasi-static calculation of Farı *et al.* (1968) which predicts satellites at 2ϵ, 3ϵ, . . .

This work has removed any serious doubt as to the nature of the alkali-rare gas low-frequency bands, of which a great number of observations have been made and several theories advanced. The essential experimental facts about such bands, all of which are consistent with the theory of Hindmarsh *et al.*, are as follows:

1. Satellites are more likely to be observed the higher the polarizability of the perturbers (i.e. the larger the value of α_d).
2. At high pressures the bands become diffuse and disappear.
3. The position of the satellite relative to the main line is almost independent of pressure and temperature (see, for example, Granier and Granier, 1966c).
4. The bands are usually several wavenumbers wide even at low pressures, but the intensity drops sharply on the low-frequency side of the satellite. In general, the more distant the band the more diffuse it is.

Recent studies of the low-frequency bands in alkalis include those of Ch'en and Wilson (1961), Ch'en and Fountain (1964), Takeo and Ch'en (1964), Jefimenko and Williams (1965) and Gwinn, Thomas and Kielkopf (1968), all of which provide data which are consistent with the idea of associating a band with a turning point in the potential well. The low-frequency bands observed by Ch'en, Atwood and Warnock (1961) on lines of indium and thallium perturbed by xenon and krypton also appear to be bands of this type. It is not, however, clear that the low-frequency satellite bands which have been observed near forbidden lines of alkalis in the presence of xenon are so easily explained. The first such observation was made by Lapp (1966), who reports an intense band in association with the weak caesium absorption line ($6S$–$5D$). This same band has been observed in emission by Gwinn, Thomas and Kielkopf (1968), and a similar band near the rubidium absorption line ($5S$–$4D$) (Besombes, Granier and Granier, 1969). No adequate theoretical treatment of this phenomenon is available.

The remaining feature of foreign gas-broadened spectral lines which is to be discussed is the appearance, usually at high perturber density, of satellite bands on the high-frequency wing of a collision-broadened line. Most work on this topic has been carried out on the resonance lines of xenon, mercury and the alkali metals. The main features of these bands are:

1. They are fainter than low-frequency bands.
2. The heavier the perturber, the closer the high-frequency band is to the main line, although in general they are much further from the line centre than low-frequency bands.
3. For a given atom pair, the high-frequency band separation is less for higher members of the principal series, and low series members usually show a second, fainter band.
4. Structure is occasionally observed (Robin, 1957).
5. The position of the high-frequency band appears to be temperature and pressure dependent (Besombes *et al.*, 1969).

Ch'en and Wilson (1961) and Ch'en, Atwood and Warnock (1961) give a comprehensive survey of band positions.

Michels *et al.* (1956, 1957, 1959a, b) have studied the shape of the absorption line of mercury at λ2537 ($^1S_0$–$^3P_1$) under the influence of helium, neon, argon and krypton at pressures of several hundred atmospheres. In every case, features are found in the high-frequency wing. With helium as perturbing gas, a shoulder develops at 225 cm^{-1} from the line when the relative density exceeds 150. This is attributed by the authors to a locally increased absorption at frequencies corresponding to the minimum in the ground state (12,6) potential, where the radial distribution of perturbers has a maximum. Neon has a similar effect on the line, producing at pressures in excess of 200 atm a pronounced high-frequency shoulder at 235 cm^{-1}.

With argon and krypton, the situation is rather different. Argon produces two high-frequency satellites at 86 and 170 cm^{-1}, krypton three at 34, 73 and 128 cm^{-1}. In both cases, the whole pattern shifts to a lower frequency in the same way as the pressure is increased, maintaining approximately constant peak-to-peak separations. These results have been interpreted by Michels, de Kluiver and Ten Seldam (1959b) in terms of weakly bound mercury-inert gas molecules. They estimate the contribution to the absorption coefficient from such molecules to be considerable in some cases, and find that this model is compatible with the measured variation of satellite intensity with temperature and perturber density. Taking a suitable potential, the high-frequency wings of the outer satellites of mercury/argon and mercury/krypton are described as a result of transitions from the lowest vibrational level of the ground state to the repulsive part of the upper state.

Granier and Granier (1965b) have also studied the mercury 2537Å/helium high-frequency satellite, and find that the satellite separation (at low densities approximately 125 cm^{-1}) increases with temperature at constant density, and with density at constant temperature. These results are not inconsistent with the ideas of Leycuras (1966) that the high-frequency satellites are formed as the result of adding to the line frequency a frequency $\Delta\nu p$, which is the oscillation frequency due to the local perturbation of the charge cloud of the perturber by the optical electron of the active atom.

The resonance line of xenon, λ1469, perturbed by hydrogen and rare gases has been investigated by Granier, Castex, Granier and Romand (1967) in absorption, and in emission at low density by Rupin and Robin (1964). Their results give the satellite band positions in cm^{-1} as

	Granier *et al.*	Rupin and Robin
Xe-H_2	170; 350	—
Xe-He	160; 300	not observed (density too low)
Xe-Ne	140; 270	162; 255
Xe-A	105; 250	102; 246
Xe-Kr	—	42; 171

A tentative explanation of these bands has been offered by Marteau, Granier, Vu and Vodar (1967), who suggest that they may arise by combination transitions between the electronic resonance line and translational bands. In support of this they offer measurements of the frequency maxima of translational bands for the pairs Xe–He (160 cm^{-1}), Xe–Ne (125 cm^{-1}) and Xe–A (65 cm^{-1}), although no firm conclusion is possible as these latter results were obtained at pressures at least one hundred times greater than the pressures used in the collision broadening experiments.

Most of the work on high-frequency satellite bands has been with the alkalimetals. Robin (1957), for example, studied the effect of high pressures of argon and nitrogen on the resonance lines of potassium, rubidium and caesium, and found that there is very little difference between the effect of the two perturbers, although nitrogen, the lighter gas, produces rather more distant satellites. In each case the satellite relative to the line appeared to move initially to a low frequency, then back again as the pressure changed.

Ch'en and Wilson (1961) have attempted an explanation of the systematics of the high-frequency bands in the principal series of lithium perturbed by helium, using the idea of an adiabatically split repulsive potential as proposed by Klein and Margenau (1959). The positions which they estimate seem to be satisfactory, but the intensity is incorrect. Jefimenko and Williams (1965) found high-frequency satellites associated with each of the first three potassium doublets formed in absorption in atmospheres of foreign gas. The resonance line bands were very diffuse; those at the second and third doublets much more intense. Jefimenko *et al.* attribute these bands to peculiarities in the potential curves during collision, an explanation which Granier and Granier (1966d) also feel is likely to be correct for the rubidium–neon high-frequency bands which they investigated. Their evidence suggests that each of the two components of the rubidium resonance doublet has associated with it one of the two observed high-frequency satellites. Most principal series doublets, however, seem to give only a single high-frequency satellite, although structure is sometimes observed in the satellite. On the other hand, Ch'en, Smith and Takeo (1960) report that in sharp series each component of the doublet has its own high-frequency satellite.

High-frequency satellites associated with the first forbidden doublet of rubidium ($5S$–$4D$) at 5167Å have been observed by Besombes, Granier and Granier (1970). Three high-frequency satellites are observed with helium as perturber and two with each of the other rare gases. The high intensity of these satellites compared to the line itself leads Besombes *et al.* to feel that, as with "forbidden" low-frequency satellites, a simple explanation in terms of potential curves is not sufficient.

The theoretical understanding of the high-frequency satellite bands is so far very incomplete. The possibility that, like the low-frequency bands, they arise from turning points in the difference potential cannot be ruled out. The difficulty is that rather little is known about the detailed shape of the interatomic potential at the close distances which must be responsible for the formation of high-frequency bands.

It is appropriate that this review should end on a note of uncertainty. Much has been discovered over the past three-quarters of a century; but the phenomenon of pressure broadening continues to bring to the surface problems of real significance for our understanding of the interactions of atoms with each other and with electromagnetic radiation.

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